

AD-A113 498

ALTUS CORP SAN JOSE CA

F/G 10/3

HIGH ENERGY DENSITY BATTERY LITHIUM THIONYL CHLORIDE IMPROVED R-ETC(U)

DEC 81 A E ZOLLA

N66001-81-C-0310

UNCLASSIFIED

0737R-1

NOSC-CR-111

NL

1 of 1
AD-A
113498

NOSC

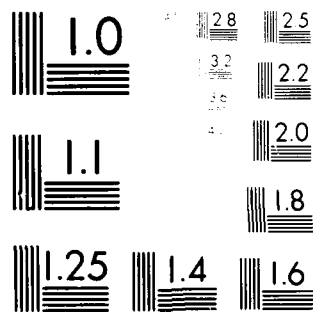
END

DATE

FILED

04-82

DTIC



Modèle de résolution N° 151 - 1944
N° 151 - 1944

12

NOSC

NOSC CR 111

NOSC CR 111

Contractor Report 111

HIGH ENERGY DENSITY BATTERY LITHIUM THIONYL CHLORIDE IMPROVED REVERSE VOLTAGE DESIGN

Dr. A. E. Zolla
Altus Corporation
1610 Crane Court
San Jose, CA 95112
Contract N66001-81-C-0310

December 1981

Final Report December, 1981

DTIC
ELECTE

APR 14 1982

Approved for public release; distribution unlimited

NAVAL OCEAN SYSTEMS CENTER
SAN DIEGO, CALIFORNIA 92152

E

AD A113498

DTIC FILE COPY



NAVAL OCEAN SYSTEMS CENTER, SAN DIEGO, CA 92152

AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

SL GUILLE, CAPT, USN

Commander

HL BLOOD

Technical Director

ADMINISTRATIVE INFORMATION

Work was done under 62711N, F11111, XF11111801/634-EM01, by Transducer
Lab Branch (Code 7121).

Released by
DL Carson, Head
Sensors and Spatial Processing
Division

Under authority of
HA Schenck, Head
Undersea Surveillance
Department

HIGH ENERGY DENSITY BATTERY
LITHIUM THIONYL CHLORIDE
IMPROVED REVERSE VOLTAGE DESIGN

FINAL REPORT
DECEMBER, 1981

CONTRACT N66001-81-C-0310

NAVAL OCEAN SYSTEMS CENTER
SAN DIEGO, CA, 92152

Dr. A.E. Zolla
ALTUS CORPORATION
1610 Crane Court
San Jose, CA 95112

REPORT NO. 0737R-1

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A	



(UNCLASSIFIED)

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NOSC CR 111	2. GOVT ACCESSION NO. AD-A113498	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) High Energy Density Battery Lithium Thionyl Chloride Improved Reverse Voltage Design	5. TYPE OF REPORT & PERIOD COVERED Final 6/81 - 12/81	
	6. PERFORMING ORG. REPORT NUMBER 0737R-1	
7. AUTHOR(s) Dr. Andrian E. Zolla	8. CONTRACT OR GRANT NUMBER(s) N66001-81-C-0310	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Altus Corporation 1610 Crane Court San Jose, CA 95112	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS Naval Ocean Systems Center 271 Catalina Blvd. San Diego, CA 92152	12. REPORT DATE December 1981	
	13. NUMBER OF PAGES 50	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report) Unclassified	
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Lithium Battery Lithium Thionyl Chloride High Energy Density Battery Voltage Reversal Battery Safety		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A test program was conducted to demonstrate safety under voltage reversal conditions of the Altus 1400 AH HEDB cell. Eight cells of an improve Anode Grid Design, all cathode (carbon) limited, were forced discharged for 150% of their normal capacity. Minor design variations were tested at 6 amp, 20°C and 12 amp, 0°C with a lithium reference electrode and separate monitoring of current through the internal reverse voltage current shunt feature. There were no ventings and no appreciable increase in cell temperature or internal pressure.		

(UNCLASSIFIED)

Table of Contents

<u>Section</u>	<u>Title</u>	<u>Page</u>
1.	Summary	1
2.	Introduction	3
3.	Background	3
4.	Design and Test Programs	5
5.	Test Results	15
5.1	Cell 192	15
5.2	Cell 193	16
5.3	Cell 194	17
5.4	Cell 195	17
5.5	Cell 196	18
5.6	Cell 197	19
5.7	Cell 198	20
5.8	Cell 199	21
6.	Capacity	47
7.	Technical Conclusions	47
8.	Recommendations	49

List of Figures

		<u>PAGE</u>
1.	HEDB Battery Concept	4
2.	Family of 17 Inch Diameter Cells	6
3.	Design and Test Plan	9
4.	Design Criteria for 150% Reverse Voltage Capability	10
5.	Test Circuit Diagram	11
6.	Actual Test Schedule	13
7.	Cell Weights and Polarization Data	14
8.	Cell Voltage/ Shunted Current	Cell 192 22
9.	Reference Electrode Data	Cell 192 23
10.	Temperature/Pressure Data	Cell 192 24
11.	Cell Voltage/Shunted Current	Cell 193 25
12.	Reference Electrode Data	Cell 193 26
13.	Temperature/Pressure Data	Cell 193 27
14.	Cell Voltage/Shunted Current	Cell 194 28
15.	Reference Electrode Data	Cell 194 29
16.	Temperature/Pressure Data	Cell 194 30
17.	Cell Voltage/Shunted Current	Cell 195 31
18.	Reference Electrode Data	Cell 195 32
19.	Temperature/Pressure Data	Cell 195 33
20.	Cell Voltage/Shunted Current	Cell 196 34
21.	Reference Electrode Data	Cell 196 35
22.	Temperature/Pressure Data	Cell 196 36
23.	Voltage/Current/Temperature/Pressure	Cell 197 37
24.	Cell Voltage/Shunted Current	Cell 198 38

List of Figures

(continued)

		<u>PAGE</u>
25.	Reference Electrode Data	Cell 198 39
26.	Temperature/Pressure Data	Cell 198 40
27.	Cell Voltage/Shunted Current	Cell 199 41
28.	Reference Electrode Data	Cell 199 42
29.	Temperature/Pressure Data	Cell 199 43
30.	Performance Summary	Cells 192 and 195 44
31.	Performance Summary	Cells 196 and 199 45
32.	Reverse Voltage Data Summary	46

1. SUMMARY

The basic design of a fully characterized 1400 AH lithium-thionyl chloride cell (High Energy Density Battery - HEDB) was modified in the grid structure of each of the electrodes to extend the capability of the cell to reliably and safely sustain a voltage reversal condition after passing through zero volts for 150% of its rated capacity without venting or explosion. Eight cells were constructed of three minor design variations, all with cell life limited by the carbon cathode, and tested at two operating conditions (a) 6 amps (0.45 mA/cm^2) constant current at an ambient temperature environment ($16\text{--}30^\circ\text{C}$) and (b) 12 amps (0.9 mA/cm^2) constant current at 0°C . Each of the eight cells were internally equipped with a switch mechanism which shunted the forced discharge current in reverse voltage similar to all previous HEDB cells tested. Each cell contained a Li/Li^+ reference electrode to monitor electrode potentials, the internally shunted current was externally monitored by bringing out one side of the switch through a dedicated electrical feedthrough terminal, and the cell internal pressure was measured by a pressure transducer built into each cell.

Full test data was obtained for seven of the eight cells built and were consistent in that-

- The maximum voltage on load was 3.46 ± 0.01 volts at 6 amps/ 21°C and 3.29 ± 0.03 volts at 12 amps/ 0°C . Anode polarization contributed 50 mV with respect to Li/Li^+ at 6 amps and 80 mV at 12 amps.
- End of cell life came rapidly after reaching 3.2 volts at 6 amps/ 21°C and 2.8 volts at 12 amps/ 0°C .
- Cell voltage in voltage reversal clamped to -0.066 volts at 6 amps/ 21°C and at -0.120 volts at 12 amps/ 0°C . Cathode potential in RV was -0.020 volts and the anode + 0.046 volts (6 amps) or + 0.100 volts (12 amps) with respect to Li/Li^+ .

- The internal RV switch shunted 2/3 of the forced discharge current in voltage reversal.
- The cell internal pressure did not increase in RV and remained at 20 psig (6 amps/21°C) or 4 ± 2 psig (12 amps/0°C).
- Cell surface temperature followed ambient except for a temporary 4°C excursion at end of cell life.
- The series of cells tested demonstrated the capability of the carbon cathode limited HEDB cell to reliably withstand 2100 AH in voltage reversal with no adverse effects observable.

2. INTRODUCTION

The scope of this contract effort was design improvement and testing to perfect reliable reverse voltage performance of the 17" diameter Lithium Thionyl Chloride High Energy Density Battery (HEDB) cell that has been previously developed by Altus Corporation under NAVY (Naval Ocean Systems Center/NAVELEX 612) sponsorship. The basic cell is 1400AH in a 1 3/8" high stainless steel case and weighs approximately 29 pounds per cell.

The test criteria, established by the Naval Surface Weapons Center, White Oak, MD, was 150% of forward capacity in a reverse voltage condition. Eight cells were built with the same internal reverse voltage chemical switch mechanism previously perfected by Altus, but with an improved anode grid current collector added, and a lithium rich design in all cases. Design variations among these eight test cells included cathode thickness to vary amount of excess lithium, and electrochemical switch thickness to optimize minimum cell height and therefore retain high energy density.

All cells but one were tested to 150% of nominal 1400AH capacity and in all cases there was with no temperature or pressure rise, no ventings or explosions. One cell was taken off test for a three-week period after 20% in voltage reversal. When forced current was reapplied, the discharged cell had high internal resistance and did not pass current.

The cells were tested under a variety of temperature, discharge rate, and simulated battery stack fixture pressure conditions.

3. BACKGROUND

Over a 3-year period the Navy, through NOSC has funded Altus to develop and characterize a lithium/thionyl chloride active cell of capacity in the range 1000 to 2000AH and a 10-year active shelf life. This cell will be incorporated into a High Energy Density Battery, HEDB, with configurations up to 150-200 KWH energy for use in underwater instrumentation packages, surface buoys, and undersea vehicles where safety, operation in any orientation, and structural strength

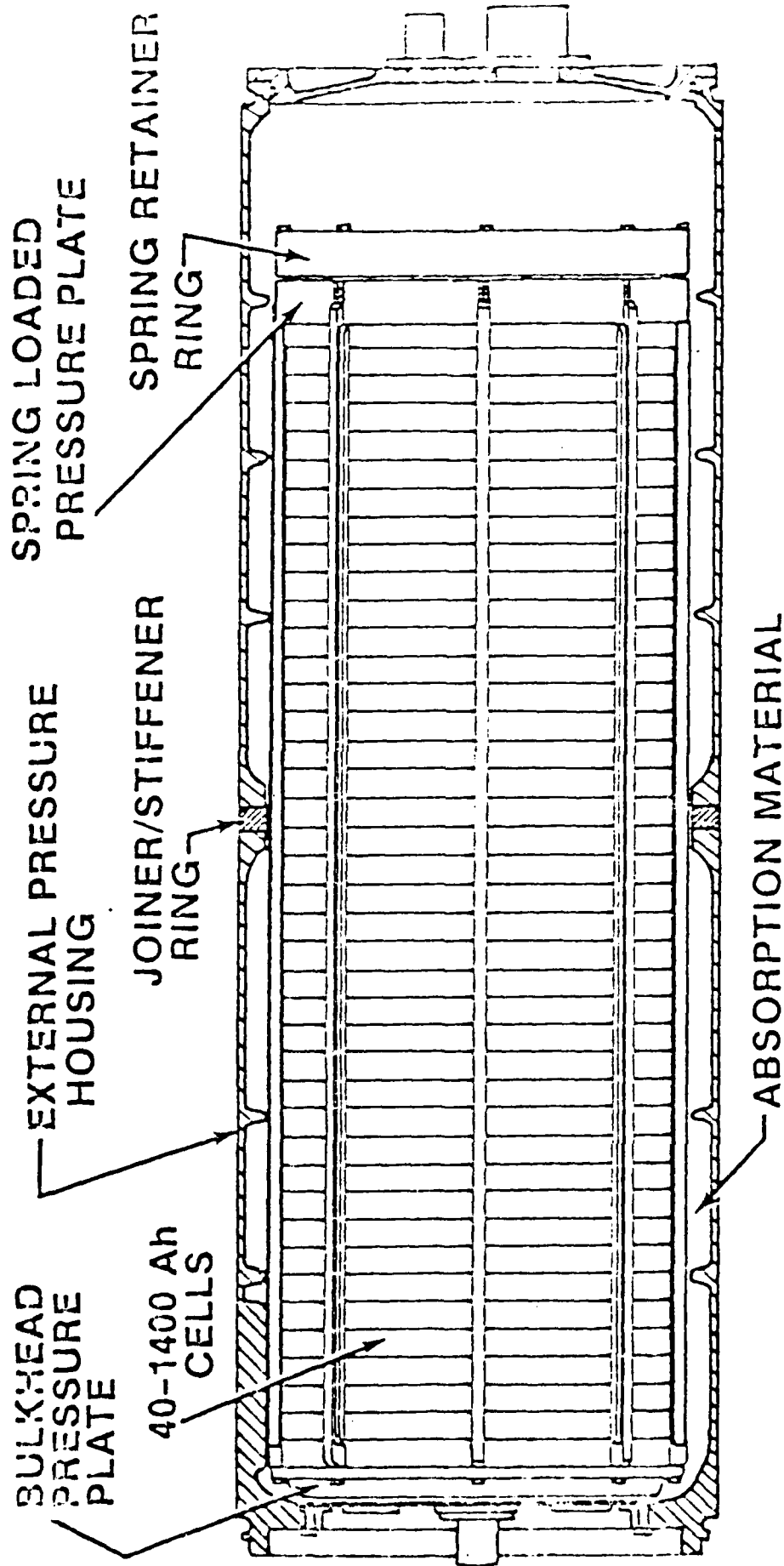


FIGURE 1

HEDB CONTAINMENT STRUCTURE

and hermeticity are key factors. The HEDB battery concept is shown in Figure 1 in which 40 cells of 1400AH capacity are arranged in series within a pressure housing.

The 1400AH cell is disc shaped and has a diameter of 17" and a thickness of 1-3/8" with a center hole of 2-5/8" diameter which houses the electrode terminals and is depicted in Figure 2. The cell weighs 29 pounds for 4.8 KWH output and is optimized for currents up to 15 amperes. The HEDB cell basic design can also be scaled to other capacities as required by the application. On other programs, cells 2 inches thick and weighing 39 pounds for a capacity of 2000AH and 7.3 KWH, and also a 17" diameter cylinder of height 7" and weighing 125 pounds for 8000AH and 28 KWH capacity have been built and tested. All 3 cell sizes are optimized for discharge rates of 100 hours or longer and a long 10-year shelf life.

Altus has now built 200 cells of 1400AH capacity under the Navy HEDB sponsorship, and 50 cells of 2000AH capacity on another program and has characterized this technology extensively for performance under a variety of operating rates, temperatures and for safety under a broad range of abusive conditions for various states of cell discharge. The cells are filled with high purity thionyl chloride electrolyte at the factory, hermetically sealed, and shipped in an active, sealed state.

4. DESIGN AND TEST PROGRAMS

The objective of this study was to extend the capability of the 1400AH HEDB cell to reliably withstand a prolonged reverse voltage condition of 1400AH beyond zero volts with testing to 2100AH in reversal to demonstrate the safety margin of the improved design. In order to achieve this level of performance, design changes were made and parameters monitored on test to verify the following:

- Each lithium anode disc was firmly attached to a nickel Exmet current collector to eliminate the possibility of hot spots developing as the lithium is utilized and when the anodes become extremely thin in reverse voltage.

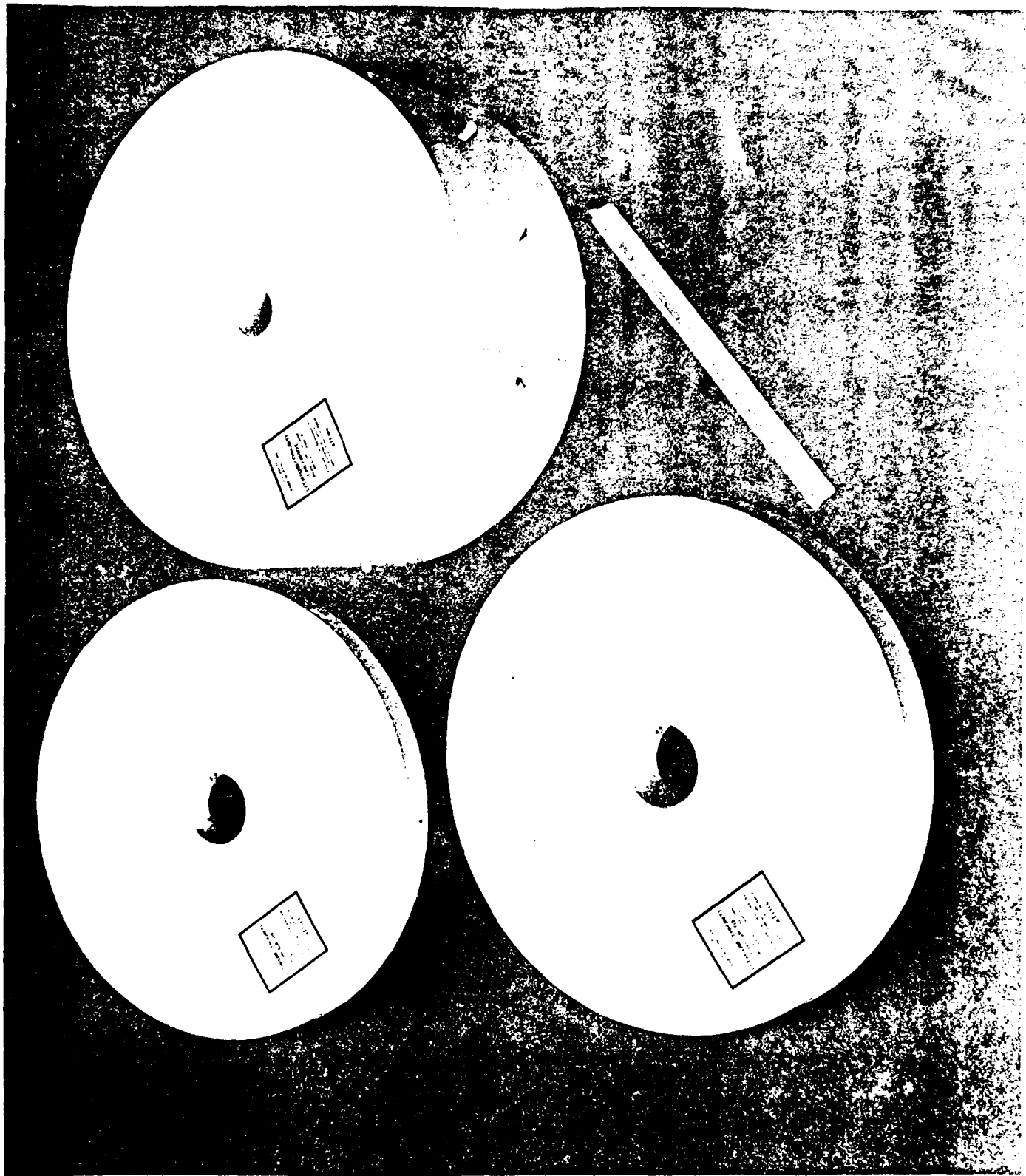


FIGURE 1

- The cathode current collector grids within the carbon cathodes were made entirely from stainless steel and nickel components were eliminated. This minimizes the lithium plating to the cathode grid structure during voltage reversal.
- The design was verified to be carbon cathode limited with both an excess of lithium at the anodes and excess of thionyl chloride within the cathode and separator void space. Throughout this design study the capacity of the cell was limited to below 1400AH by the carbon weight and sufficient lithium was made available for 1800AH capacity and sufficient thionyl chloride for 2000AH capacity.

The cells were specially equipped with two extra ceramic-to-metal electrical feedthrough assemblies in addition to the two normal anode and cathode electrode terminals. The extra terminals were used for experimental purposes.

- One terminal permitted monitoring of a lithium reference electrode incorporated into the cell in order to follow the behaviour of the anode and cathode potentials separately with respect to Li/Li^+ and verify cathode polarization being responsible for end of cell life.
- The second extra feedthrough was internally connected to one end of the reverse-voltage switch incorporated into all HEDB cells. This switch feature, comprised of materials compatible with the cell chemistry, is normally connected across the anode and cathode, but in these experimental cells the return connections to the cathode was made via the extra feedthrough and an external one milliohm current shunt back to the cathode terminal. In this manner the operation of the internal RV switch could be monitored and its efficiency and low impedance established throughout the discharge tests.

The first four cells built in this study incorporated a thick heavy duty RV switch mechanism which increased the HEDB cell thickness from 1.38 inches to 1.45 inches and further increased the weight of the

cell by 324 grams. Two of the four cells (SN 194, 195) were designed to contain 80% of the standard cathode weight in order to ensure carbon cathode limitation and provide data which could be directly compared to the standard cathode cells (SN 192, 193) and verify a linear relationship between carbon weight and capacity. Each of the designs were tested at the two discharge conditions - one cell at 6 amps constant current discharge at normal ambient (20° to 27°C) temperatures and the second cell at 12 amps constant current at low temperatures (-5° to +10°C).

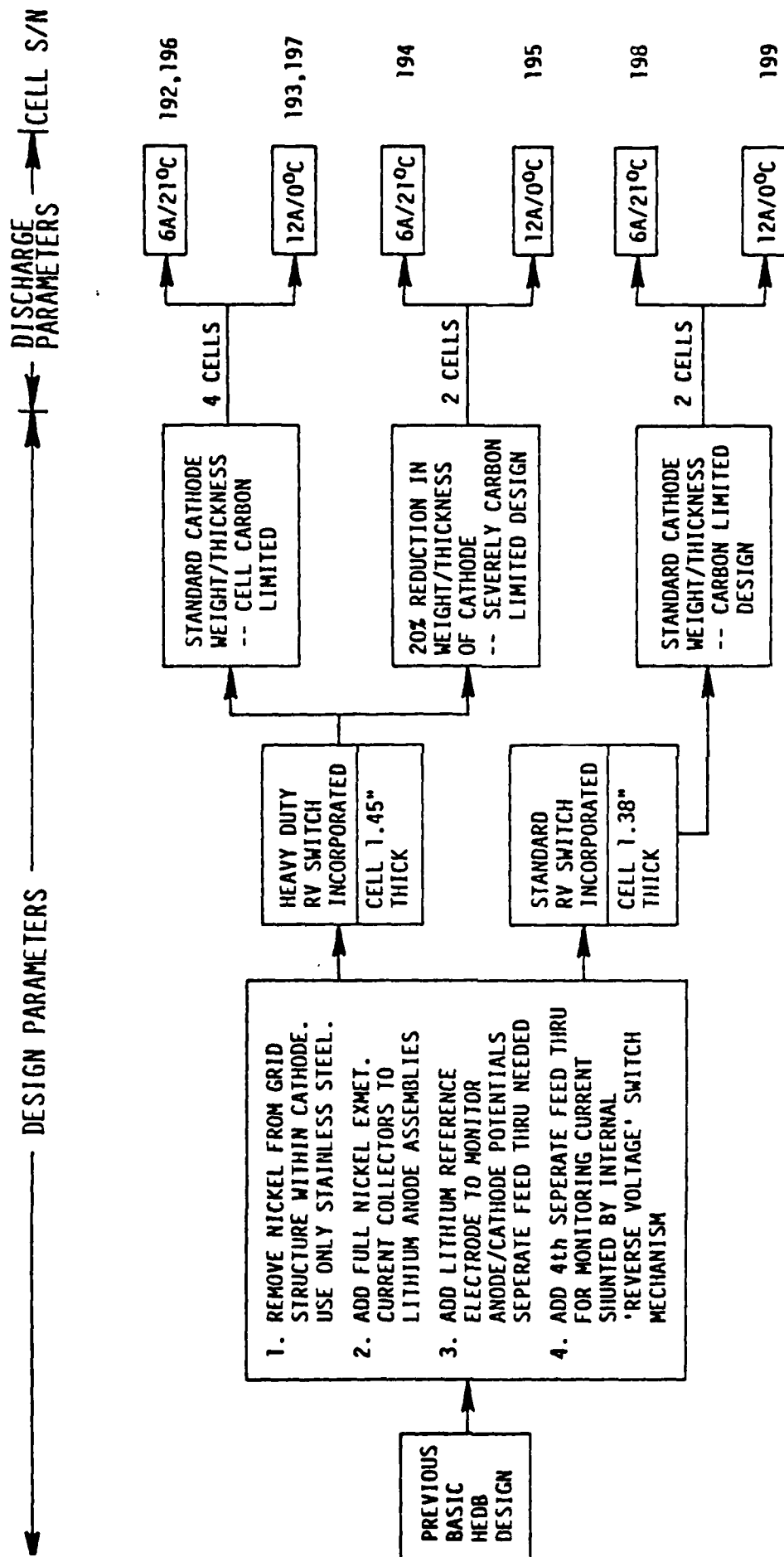
The second set of 4 cells (SN 196 to 199) were designed and constructed after the successful completion of the 150% voltage reversal tests of the first set (SN 192 to 195). It was determined from the test results that the standard weight cathode led to a carbon cathode limited design and that any further carbon weight reduction was unnecessary. The results also indicated by the successful outcome of the 4 cell testing that some reduction in the internal switch volume and weight could be achieved without sacrificing safety to extended forced discharge. Two of this next set of cells (SN 198, 199) were equipped with the standard RV switch mechanism which brought the cell thickness back to the standard 1.38 inches and the cell weight back to an acceptable 30 lbs. Once again the two operating discharge conditions 6A at ambient temperature and 12A at 0°C were used to test the two designs which varied only in the RV switch design.

The Design and Test Matrix is summarized by Figure 3 and the Design Criteria summarized in Figure 4.

The experimental modifications to the cell to achieve a four terminal output caused some loss in capacity for this series of 8 cells compared to production units previously tested.

The constant current discharge of each cell was accomplished using a power supply as shown in the circuit diagram (Figure 5) and the discharge current and internal switched current were monitored across one milliohm shunts incorporated into the circuit. Each cell was equipped with a Sensometric Pressure Transducer (0.5mV per PSIG) which permitted the cell's internal pressure to be followed. Thermo-

DESIGN AND TEST PLAN



NOTE: 6A = 0.45 mA/cm²
12A = 0.90 mA/cm²

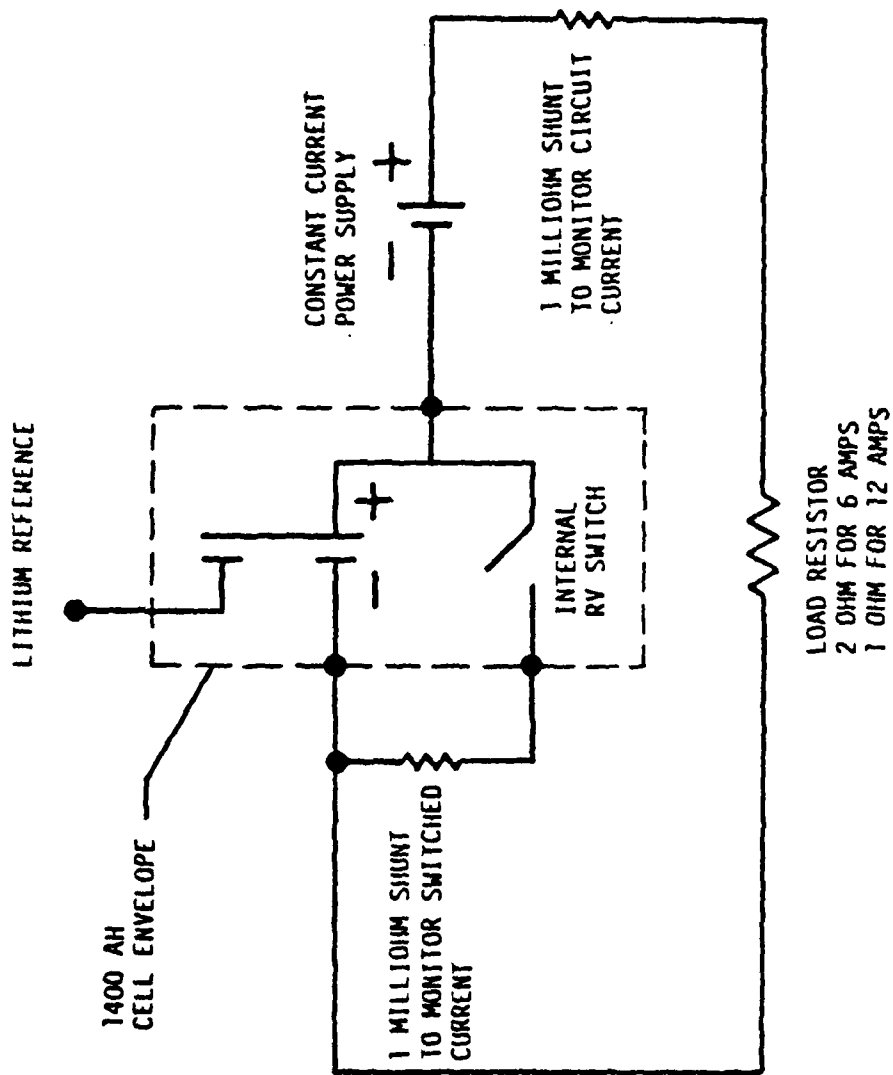
FIGURE 3

CRITERIA FOR EXTENDED RV SAFETY OF 1400 CELL

1. CAPACITY OF CELL CARBON LIMITED
2. 30% EXCESS LITHIUM ABOVE THEORETICAL OF 1400 AH
3. 45% EXCESS SOC_{12} ABOVE THEORETICAL OF 1400 AH
4. ALL LITHIUM DISC ANODES FIRMLY BONDED TO NICKEL EXMET CURRENT COLLECTOR
5. CATHODE CURRENT COLLECTOR GRIDS STAINLESS STEEL
6. A CHEMICAL SWITCH MECHANISM INCLUDED IN THE INTERNAL DESIGN TO
 - (A) SHUNT > 70% OF FORCED DISCHARGE CURRENT IN REVERSE VOLTAGE
 - (B) CLAMP CELL NEGATIVE VOLTAGE TO LOW VALUES THROUGH THE LOW SWITCH IMPEDANCE OF 15 MILLIOHMS

NOTE: CELL WEIGHT OF 31 POUNDS IS MAINTAINED EVEN WITH RV SAFETY FEATURES ABOVE.

FIGURE 4



HEDB TEST CIRCUIT DIAGRAM

FIGURE 5

couples both in the test chamber and affixed to the cell surface gave temperature data. The emf between lithium reference and both anode and cathode terminals gave data on internal polarization effects. The following parameters were recorded using a Fluke 240A Datalogger recording at 30 minute intervals.

- Cell (cathode versus anode) voltage
- Anode potential versus lithium reference electrode
- Cathode potential versus lithium reference electrode
- Discharge current
- Shunted current through internal RV switch.
- Environmental temperature
- Cell surface temperature
- Cell internal pressure

In addition, strip chart recordings of voltage data were made as the cell went through zero volts into voltage reversal.

The actual test schedule of the 8 cells is summarized in Figure 6 which details the time the tests commenced, when the cell entered reversal and when, finally, the test was terminated after exceeding 2100AH in reverse voltage.

A record of the weight, volume and theoretical capacity of the electrolyte within each cell is given in Figure 7 together with total cell weights. It was noted that one cell (SN 197) received a less than normal electrolyte volume. Cells, SN 192 to 197, had an average weight of $14286 \pm 264/-541$ grams with an average electrolyte fill of 3.18 liters corresponding to a theoretical $2082 \pm 92/-105$ amp-hours of thionyl chloride for the 1.3M electrolyte. The last two cells (SN 198, 199) were lighter at 13962 ± 84 grams due to the decreased cell thickness at 1.38 inches.

Prior to discharge testing the cells were placed on a de-passivating load of 0.1 ohms for 3 minutes followed by voltage checks at lighter loads to 0.75 ohms. The voltage data for this polarization check are given for each cell in Figure 7. The low voltage output of cell 197 on the 0.1 ohm load further indicated some abnormality of this par-

HEDB TEST SCHEDULE (8.10.81 Through 10.24.81)

Cell Serial Number	Started Test	Passed Through Zero Volts	Hours On Normal Discharge	Ended Test	Hours In Voltage Reversal
192	1400 Hrs 222 Day 8.10.81 Date	2030 Hrs 231 Day 8.19.81 Date	222.5 Hrs	1500 Hrs 246 Day 9.3.81 Date	354.5 Hrs
193	0700 Hrs 223 Day 8.11.81 Date	0030 Hrs 228 Day 8.16.81 Date	118.5 Hrs	0900 Hrs 235 Day 8.23.81 Date	176.5 Hrs
194	1530 Hrs 226 Day 8.14.81 Date	1630 Hrs 235 Day 8.23.81 Date	217 Hrs	0700 Hrs 251 Day 9.8.81 Date	374.5 Hrs
195	1230 Hrs 227 Day 8.15.81 Date	1130 Hrs 231 Day 8.19.81 Date	95 Hrs	2100 Hrs 238 Day 8.26.81 Date	177.5 Hrs
196	1330 Hrs 268 Day 9.25.81 Date	2330 Hrs 275 Day 10.2.81 Date	178 Hrs	0800 Hrs 292 Day 10.19.81 Date	392.5 Hrs
197	0700 Hrs 271 Day 9.28.81 Date	0130 Hrs 275 Day 10.2.81 Date	90.5 Hrs	1130 Hrs 275 Day 10.2.81 Date	10 Hrs
198	1300 Hrs 273 Day 9.30.81 Date	0700 Hrs 282 Day 10.9.81 Date	210 Hrs	1300 Hrs 297 Day 10.24.81 Date	366 Hrs
199	0700 Hrs 274 Day 10.1.81 Date	1100 Hrs 278 Day 10.5.81 Date	100 Hrs	0800 Hrs 286 Day 10.13.81 Date	189 Hrs

FIGURE 6

CELL WEIGHT AND POLARIZATION DATA

Cell S/N	192	193	194	195	196	197	198	199
Weight of cell prior to electrolyte fill (grams)	8950	8970	8979	8965	8890	8870	8727	8747
Weight of cell filled (grams)	14465	14550	14290	14480	14188	13745	14045	13878
Weight of electrolyte (grams)	5515	5580	5311	5515	5298	*5075	5318	5131
Calculate volume electrolyte (liters)	3.28	3.32	3.16	3.28	3.15	*3.02	3.17	3.05
Theoretical capacity of SOCl ₂ in cell (Amp-Hours)	2149	2174	2069	2149	2064	1977	2071	1999
<u>Polarization Data (volts)</u>								
0.1 ohm load for 3 minutes	3.00	3.01	2.94	3.04	2.93	*2.87	2.97	2.98
0.2 ohms	3.20	3.22	3.19	3.24	3.10	3.15	3.20	3.21
0.5 ohms	3.37	3.38	3.39	3.40	3.39	3.37	3.38	3.39
0.75 ohms	3.42	3.42	3.43	3.44	3.43	3.42	3.43	3.44

* NOTE: Cell #197 filled with a low electrolyte weight displayed a poor voltage on 0.1 ohm load.

FIGURE 7

ticular cell with regard to its internal impedance. All open circuit voltages were 3.63 ± 0.01 volts subsequent to being filled with electrolyte.

5. TEST RESULTS

5.1 Cell 192

The cell was force discharged at 5.98 amps constant current at an ambient temperature of $27 \pm 3^\circ\text{C}$. The output voltage, Figure 8, maintained a steady 3.47 volts for a long period slowly dropping to about 3.2 volts when the voltage rapidly declined, due to polarization of the cathode, & passed through zero volts after 223 hours of discharge. The cell output voltage locked up at 60 to 80 mV negative and remained at this low value until the test was terminated some 355 hours later corresponding to 2105AH of discharge in reversal.

The internal RV switch closed as the cell went into reversal as intended and, as shown in the top right of Figure 8, the shunted current attained a maximum of 4.1 amps. A change in the switch shunt impedance was observed after 115 hours of its operation when the shunted current dropped to 2.8 amps which was maintained until the end of testing.

Of the total 3434AH discharge, 1097AH were shunted internally in RV which meant the cell itself accommodated 2337AH. Since this value exceeded the theoretical capacity of lithium within the anodes it is likely that some lithium dendrites had grown between the cell's cathode and anode during voltage reversal.

The cathode and anode potentials with respect to the lithium reference electrode are shown in Figure 9. The maximum cathode potential was 3.51 volts for a minimal anode polarization of 50 millivolts. The end of cell life is clearly due to cathode polarization since the anode polarization during RV is again 50 to 60 millivolts only, whereas the cathode potentials finally falls - 0.02 volts with respect to the reference electrode at the end of test.

It is thought that the brief anode polarization peak at the end of cell life is an artifact due to the location of the reference electrode in the cell.

The temperature and pressure data, (Figure 10), show that the cell follows the ambient temperature diurnal cycles except for a brief 4°C temperature excursion during voltage decline resultant from temporary I^2R losses at the carbon cathode. The pressure at the end of cell life reached a maximum of 21 psig for a cell temperature of 32°C but returned quickly to lower pressures during voltage reversal indicating that no gas was generated in RV.

5.2 Cell 193

This cell of identical design to cell 192 was discharged at 12.05 amps at an refrigerated environmental temperature of $5^\circ \pm 5^\circ\text{C}$. The cell voltage plotted in Figure 11 attained a maximum plateau of 3.30 volts and when below 2.8 volts rapidly fell below zero volts after 119 hours of discharge. The cell voltage clamped at -0.12 volts for the entire 177 hours in voltage reversal, due to the operation of the Altus RV switch which shunted 68% of the forced discharge current through the low 15 milliohm shunt impedance. The reference voltage data of Figure 12 show a maximum cathode potential of 3.38 volts for an anode polarization of only 90 mV. Again cathode polarization is responsible for end of cell life and even after 2127Ah of RV the anode is only 100 mV polarized, with the cathode negative with respect to Li/Li^+ by 20 mV. The anode polarization peak at 114 hours is a reference electrode design artifact.

Figure 13 demonstrates the flat cell temperature of $4^\circ \pm 1^\circ\text{C}$ with the temporary cathode polarization effect at end of cell life raising the cell surface temperature 3°C. The pressure within the cell remained at 0 psig with only 1 psi increase at 0 volts.

The total amp-hours of forced discharge totalled 3555Ah with approximately 1445Ah shunted in RV by the internal switch mechanism.

5.3 Cell 194

This cell was designed with 80% of the standard cathode material built into the previous two cells (192, 193) and a severely cathode limited cell was expected.

The discharge profile at 5.88 amps and $26^{\circ} \pm 3^{\circ}\text{C}$ ambient temperature is displayed in Figure 14. In common with cell 192 the early maximum cell voltage of 3.47 volts was due to a polarization at the cathode of 140 mV and at the anode, 40 mV. The cell voltage falls rapidly below 3.2 volts and is quickly clamped in negative voltage to -0.06 volts by the operation of the internal switch which shunts up to 4.3 amps of the 5.9 amps current. The electrode reference voltage data of Figure 15 proves a cathode limited system and after 592 hours of forced discharge the test was terminated for 2183AH in RV, a cathode merely 20 mV below lithium potential, and the anode polarized only 40 mV positive.

The cell temperature followed the ambient exactly and the internal cell pressure climbed 16 psig during the normal cell discharge with no further gas generation in voltage reversal (Figure 16).

The cell withstood a total discharge of 3460AH over 592 hours with approximately 1440AH shunted internally during reverse voltage.

5.4 Cell 195

This 12 amp discharge at $0.5^{\circ} \pm 3.0^{\circ}\text{C}$ is almost identical in all respects with the discharge of cell 193 described earlier. The cell in this case was more severely carbon limited and 80% capacity was obtained compared with the standard cathode system. The internal switch operated perfectly to shunt two-thirds of the force discharge current in RV which clamped the cell to a constant low negative potential of -0.120 volts with a contribution of +90 mV from the anode and - 30 mV from the cathode both with respect to Li/Li^{+} . The cell surface temperature held at $1^{\circ} \pm$

1°C except for a cathode polarization heating to 4°C at the end of cell life. The pressure data was not recorded in this test due to a malfunction. All relevant data is to be found in Figures 17, 18 and 19.

3276AH were discharged through the cell with about 1432AH internally shunted in RV. The cell again withstood in excess of 150% reverse voltage with no deleterious effects recorded or observed.

5.5 Cell 196

This cell was of identical design to cells 192, 193 described earlier except for a relocation within the cell of the reference electrode in an attempt to remove the anomalous anode polarization peak at zero volts experienced with the first series of 4 cells. Cells 195 through 199 all had the same new design of reference electrode system.

The discharge curve of cell 196 in Figure 20 exhibits similar behaviour to that seen previously for a 6 amp discharge at ambient temperature. The operating cell voltage of 3.45 volts falls slowly to about 3.2 volts and then drops rapidly to a clamped negative voltage of 60 to 80 mV negative brought about by the timely operation of the internal RV switch at zero volts. The shunted current peaked at 4.2 amps and then settled into 4 amps for the duration of the test. The reference electrode data (Figure 21) in this case is meaningless beyond the 160 hours of normal discharge and clearly the lithium on the reference electrode has either been dissipated or severely polarized. It is not possible for the anode potential to be negative with respect to the reference electrode with no current flowing in that circuit. Figure 22 shows the cell following the $21^{\circ} \pm 4^{\circ}\text{C}$ ambient except for a 10°C rise in cell surface temperature at zero volts cell output. The cell internal pressure climbed steadily from 0 psig to 27 psig at zero volts and then falling back to a constant 24 ± 2 psig throughout voltage reversal.

5.6 Cell 197

This cell of the same design as #196 of low electrolyte fill and poor polarization curve (Figure 7) continued to operate in anomalous fashion when discharged at 12 amps at 0°C. Figure 23 is a composite plot of the data obtained. It is evident that the cell output voltage is very low and never exceeded 3.0 volts. A 3 hour voltage spike in the cell voltage curve further indicates a problem. The cell temperature at its surface continually maintained 10°C above ambient indicating an internal discharge taking place - possibly through an internal short circuit. An examination of the reference voltage curves shows that the anode is unduly polarized at 0.3 volts, where 0.1 volts is typical at these discharge conditions. The cathode potential is also 0.1 volts below normal. At the end of cell life the cell temperature rose a further 17°C compared to a usual 3 or 4°C for cells 193 and 195.

When the cell went into voltage reversal the internal switch operated normally and the cell voltage locked up although the potential at -0.03 volts was more negative than normal due to the excessive anode polarization that occurred.

Due to the sequence of abnormalities it was decided to replace this cell with another and the test on #197 was terminated. Unfortunately the replacement cell that was built had a short circuit in the reverse voltage switch feature and could not be used for this study. To remain on schedule, cell 197 was put back on test after a 3 week interruption. During this standby period the cell had presumably continued to self discharge internally and no potentials could be detected between anode and cathode or between either electrode and the lithium reference electrode. In an attempt to force discharge the cell the voltage across the cell was raised to -50 volts but no current could be drawn due to the now high impedance of the cell. The test on this cell was terminated without any venting taking place.

5.7 Cell 198

This cell and the following cell (#199) were of reduced thickness at 1.38 inches since the design incorporated the standard reverse voltage switch. All other design features of cells 192, 193, 196 and 197 were maintained. The cell was discharged at a constant 6 amps at an ambient temperature of $21^{\circ} \pm 5^{\circ}\text{C}$. The discharge characteristics were similar to the previous tests (cells - 192, 194, 196) in which the cell output of 3.46 volts held for a long period, (Figure 24) and at the end of cell life the internal switch clamped the cell output to 75 ± 5 mV negative. The reference electrode data (Figure 25) showed a 150 mV cathode polarization and a 40 mV anode polarization in the early stages of discharge. at the end of cell life the lithium reference electrode became unreliable and it seems that the electrode gradually attained the potential of the nickel grid within the original lithium reference electrode.

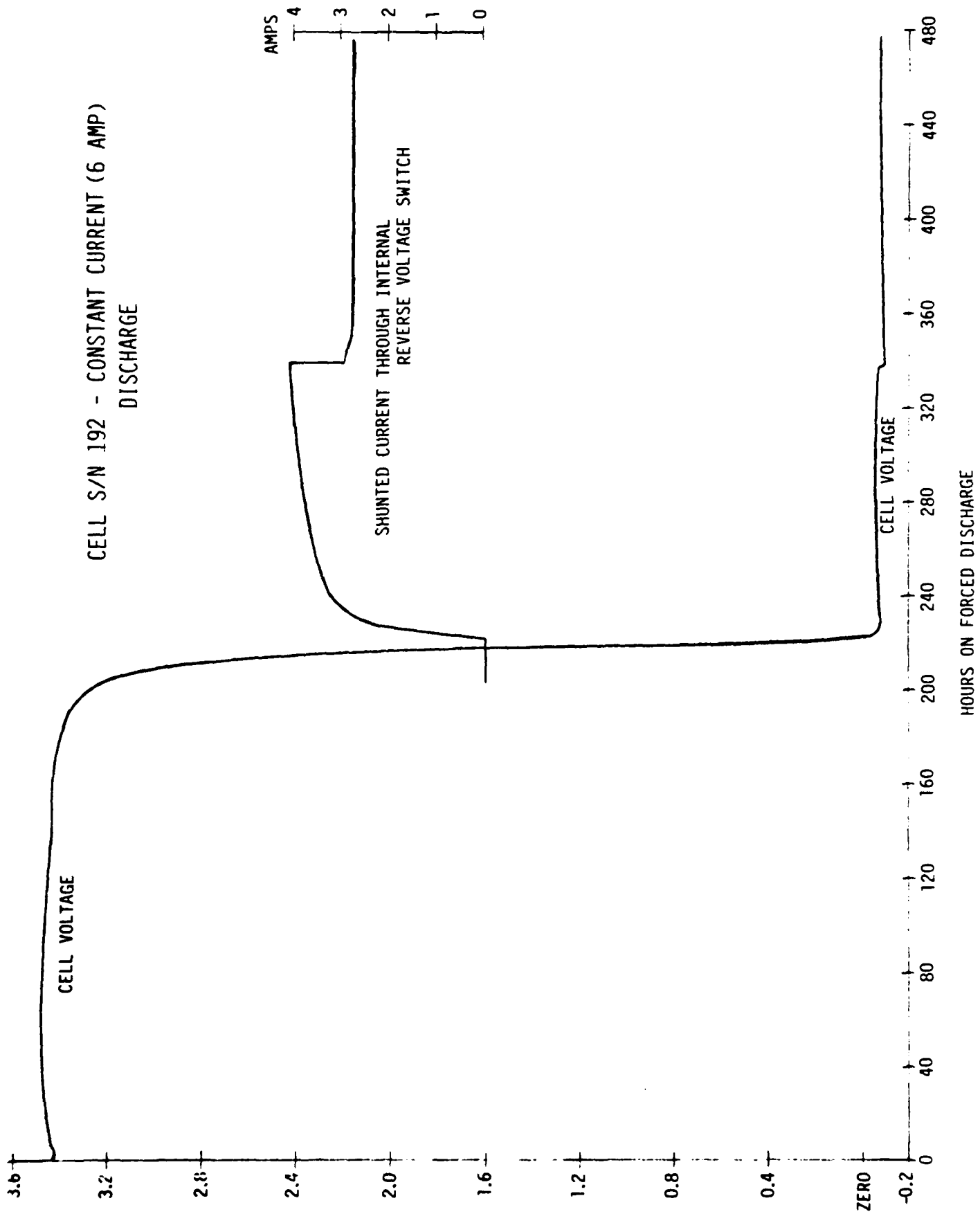
After 82 hours in voltage reversal the current shunt circuit opened either due to a fault in the external circuit or a failure internally in the switch itself. At this point the entire 6 amps was forced through the cell presumably causing lithium plating into the cathode. During the period of lithium plating, the cell voltage was constant at -0.135 ± 0.005 volts until the 343rd hour of discharge (Figure 24) when a second negative going step was observed. It is assumed this second step is the point at which the full 6 amps discharge current has totally consumed the lithium anodes and electrolysis of the electrolyte is occurring. A cell potential of about -0.38 volts was maintained until the test was terminated after 2262Ah of reverse voltage testing. Figure 26 does not indicate any abnormal temperature or pressure fluctuations throughout the 576 hour test period. There was no increase in the cell internal pressure during RV and the final pressure recorded at the end of test was 17.3 psig. The test was successful.

The following calculation supports the interpretation of the steps observed in the reverse voltage discharge curve.

- a) Amp-hours of lithium anode consumed during normal discharge to zero volts = 1257 AH
- b) Amp-hours of lithium plated into cathode from zero volts to the switch shunt opening at 82 nd hour of RV
 - = 490 AH - Shunted current
 - = 490 AH - 302 AH
 - = 188
- c) Amp-hours of lithium plated into cathode from switch failure to second break in curve 50 hours later
 - = 300 AH
- d) Total lithium consumed over the first 343 hours of testing
 - = (a) + (b) + (c)
 - = 1257 + 188 + 300
 - = 1745 AH
- e) The theoretical capacity of the anodes within this cell is 1700 AH which is very close to the 1745 AH figure calculated in (d) and indicates the step in the voltage at the 343 rd hour is due to total lithium depletion

5.8 Cell 199

This cell discharge at 11.96 amps and and $0^{\circ} \pm 2^{\circ}\text{C}$ on enviormen-
tal temperature displayed the typical charactertics found in the
earlier test. The anode polORIZATION remained low at 50 mV prior
to zero volts and 90 mV in voltage reversal with the cathode pot-
ential falling from a plateau at 3.31 volts to a clamped negative
potential of -0.04 volts during reverse voltage discharge. The
cell demonstrated carbon limitation to cell life and the internal
RV switch shunted 74% of the force discharge current. The brief
temperature excursion of the cell during voltage decline was only
 4°C and the cell pressure remained contant at 5 psig during RV.
The relevant data are to be found in Figures 27 through 29.



CELL VOLTAGE
21

FIGURE 8

CELL S/N 192 - CONSTANT CURRENT (6 AMP)
DISCHARGE

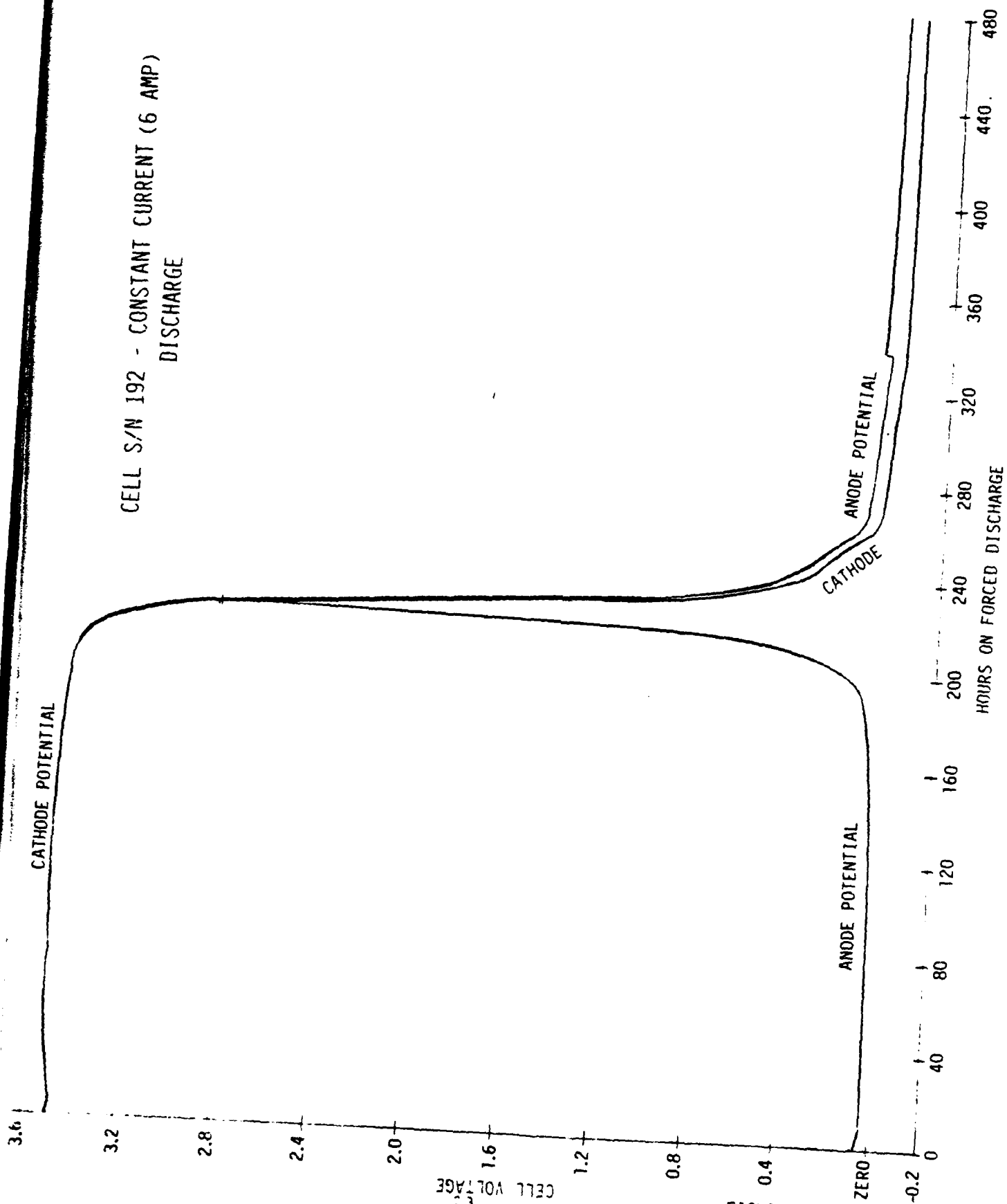


FIGURE 9

ZERO VOLTS

CELL S/N 192 - CONSTANT CURRENT (6 AMP)
DISCHARGE

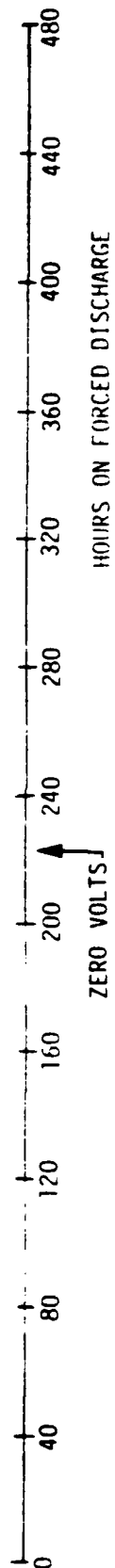
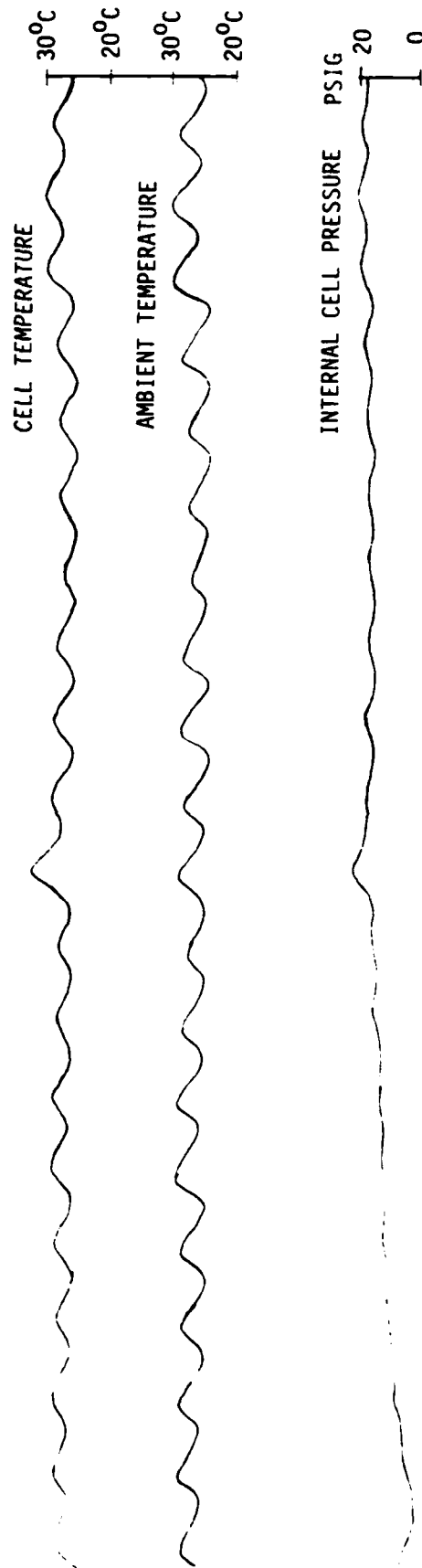
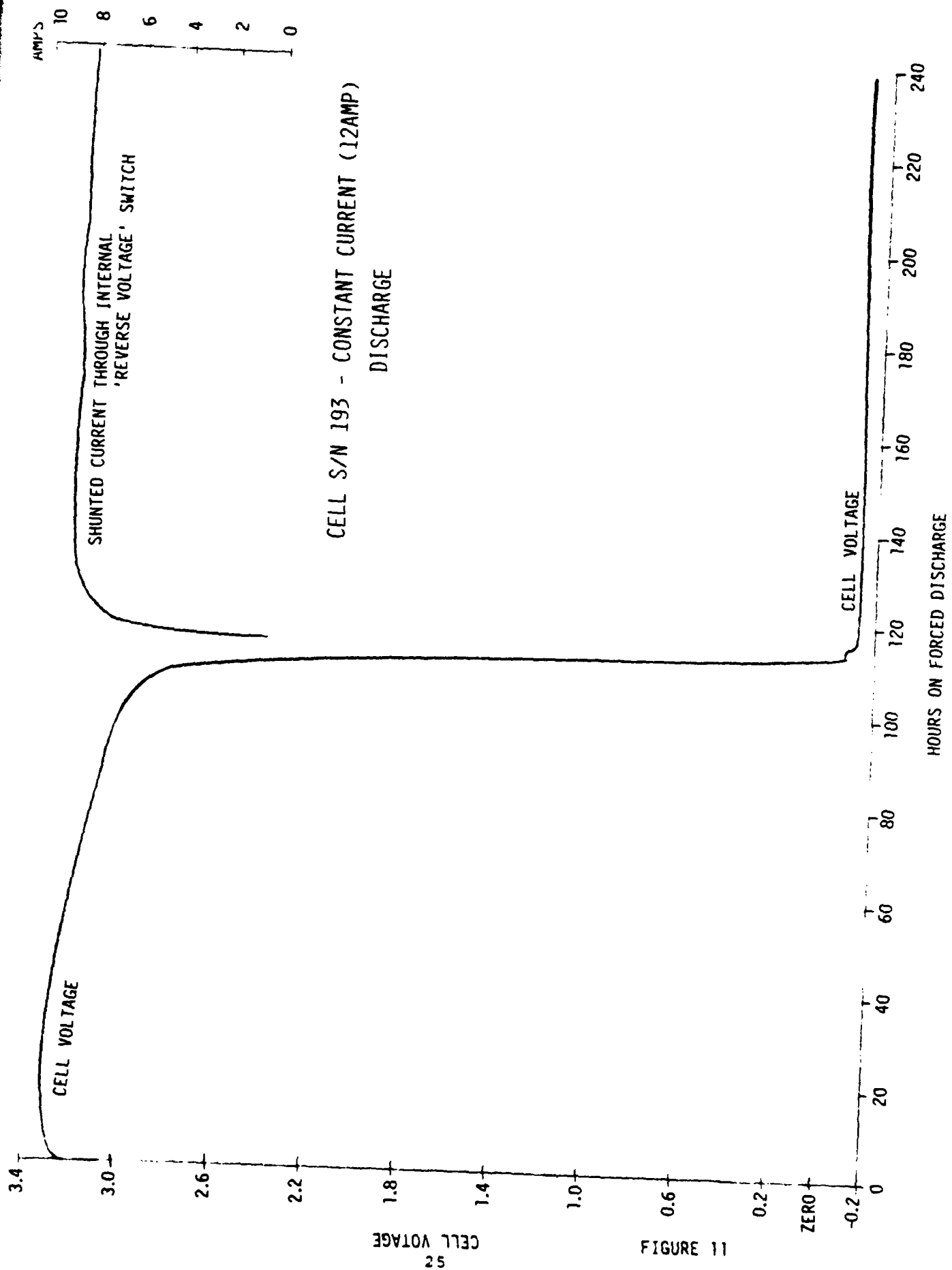


FIGURE 10



CELL VOLTAGE

FIGURE 11

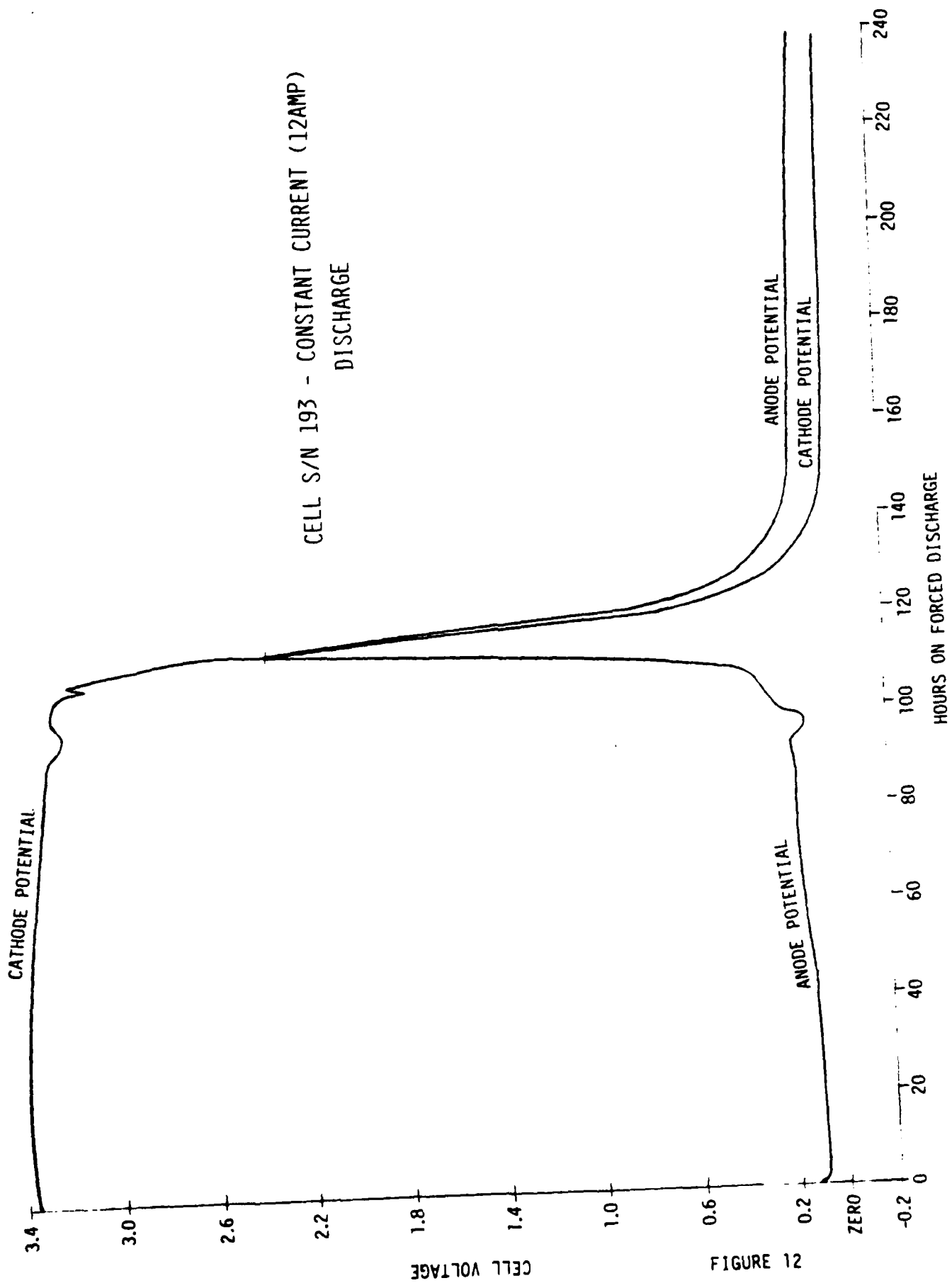


FIGURE 12

ZERO VOLTS

CELL S/N 193 - CONSTANT CURRENT (12AMP)
DISCHARGE

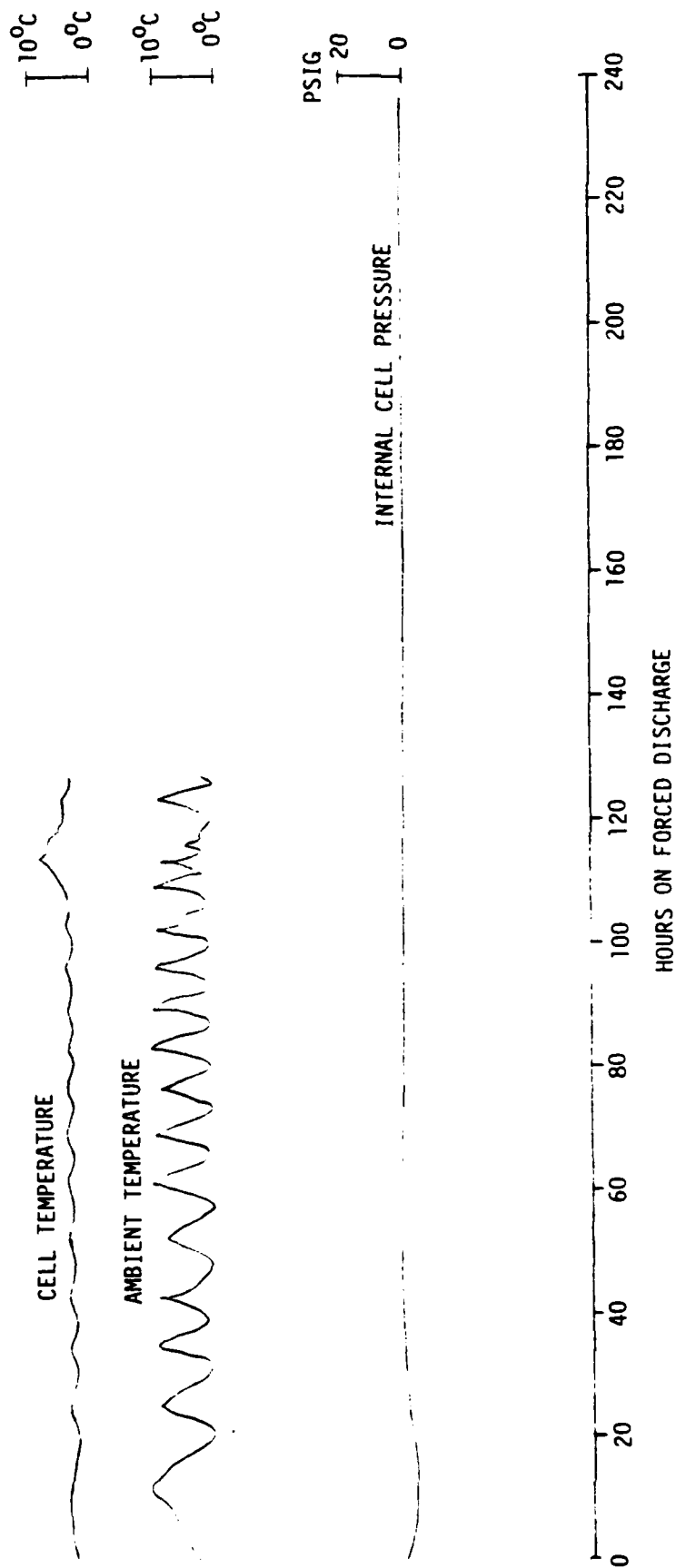


FIGURE 13

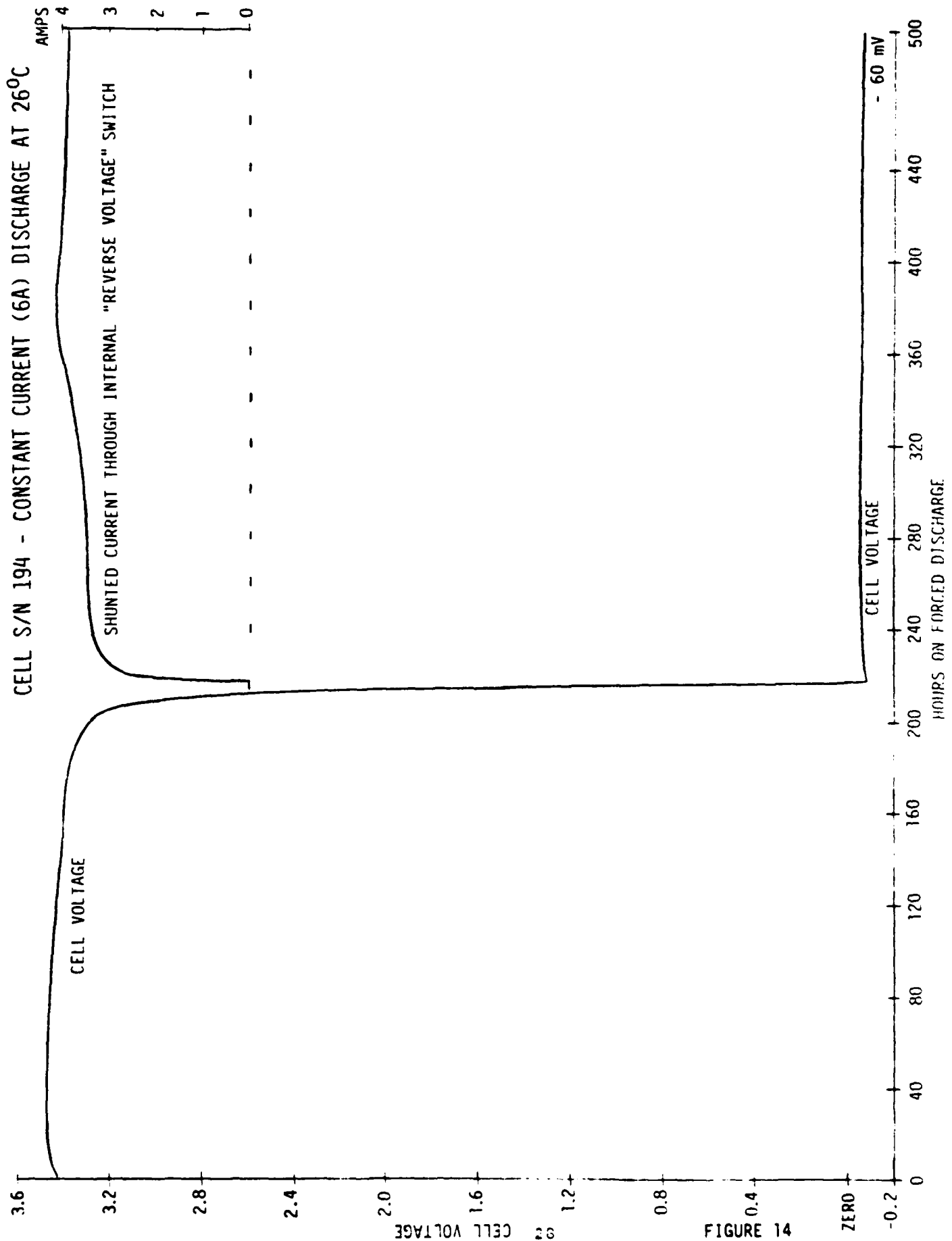


FIGURE 14

CELL S/N 194 - CONSTANT CURRENT (6A) AT 26°C

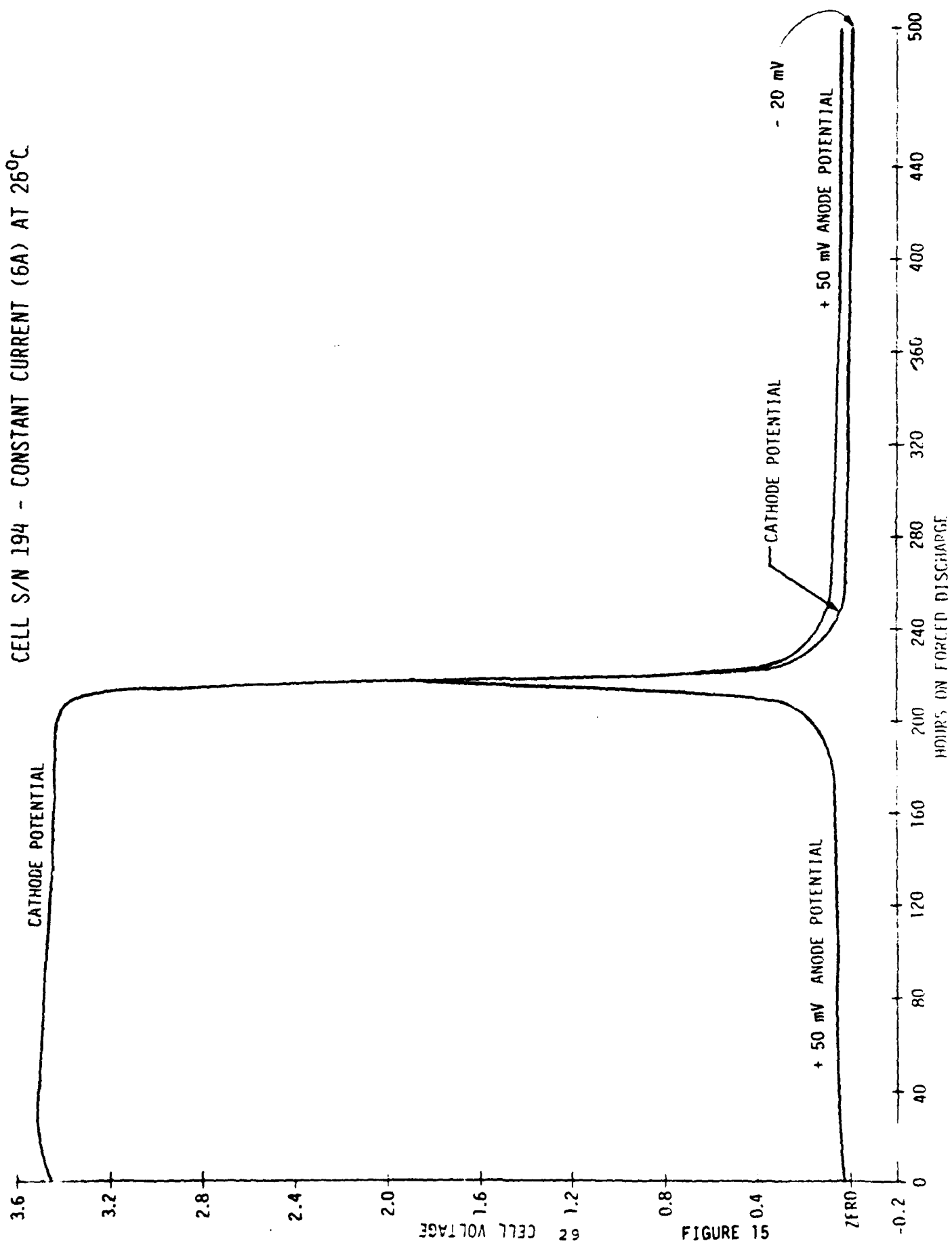


FIGURE 15

CELL S/N 194 - CONSTANT CURRENT (6A) DISCHARGE

END OF CELL LIFE

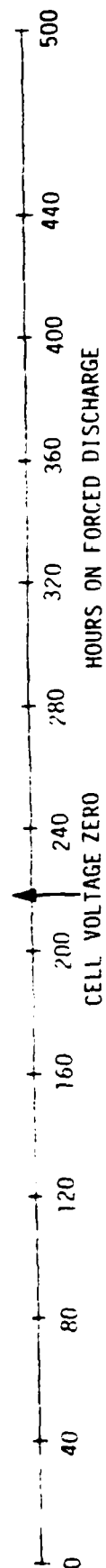
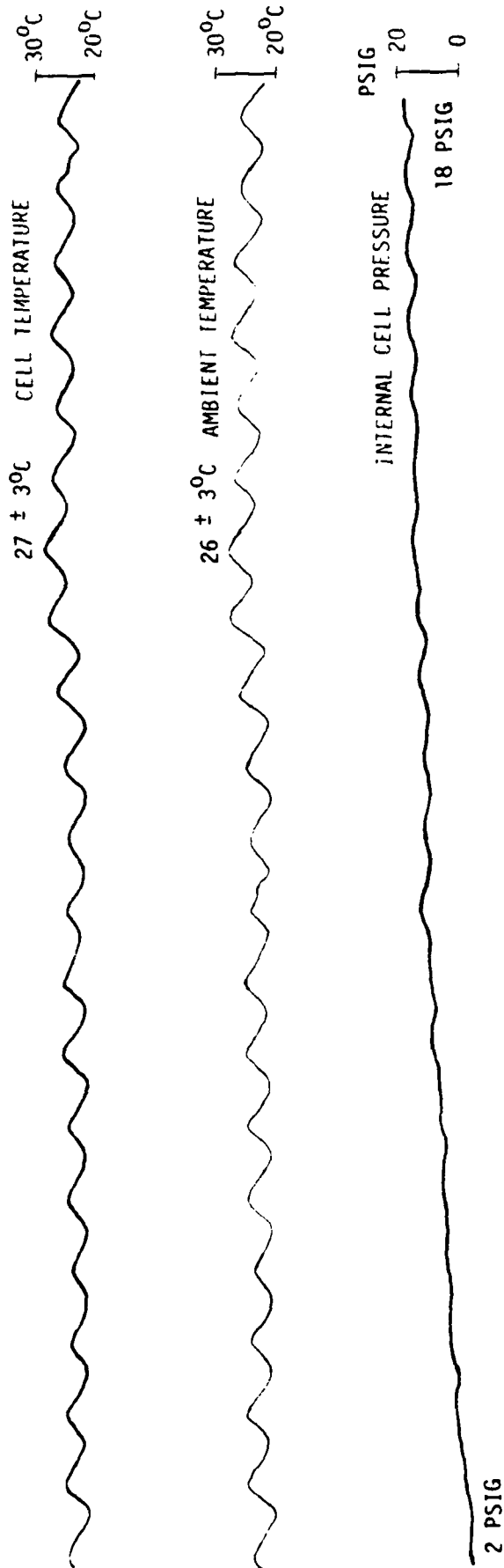


FIGURE 16

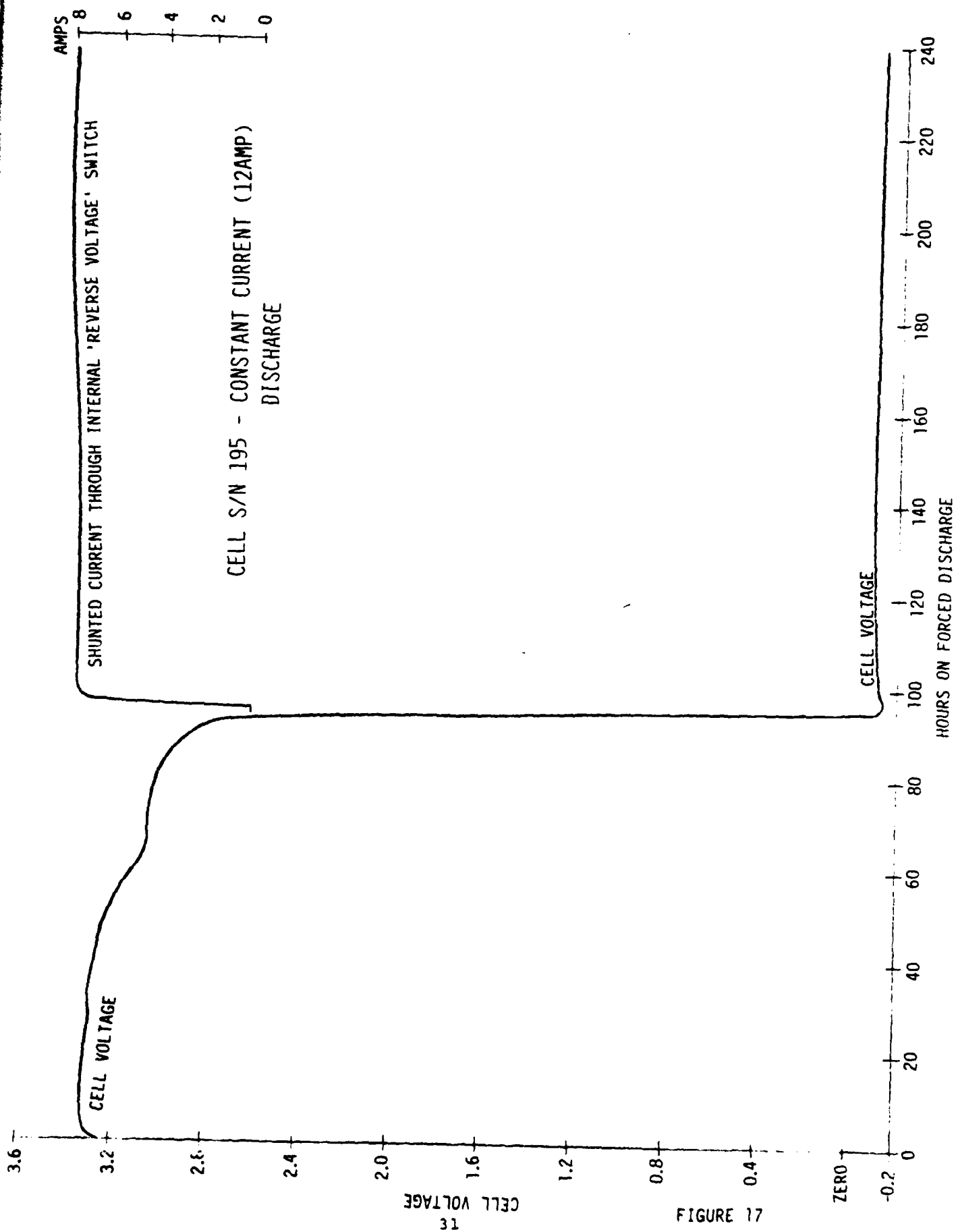
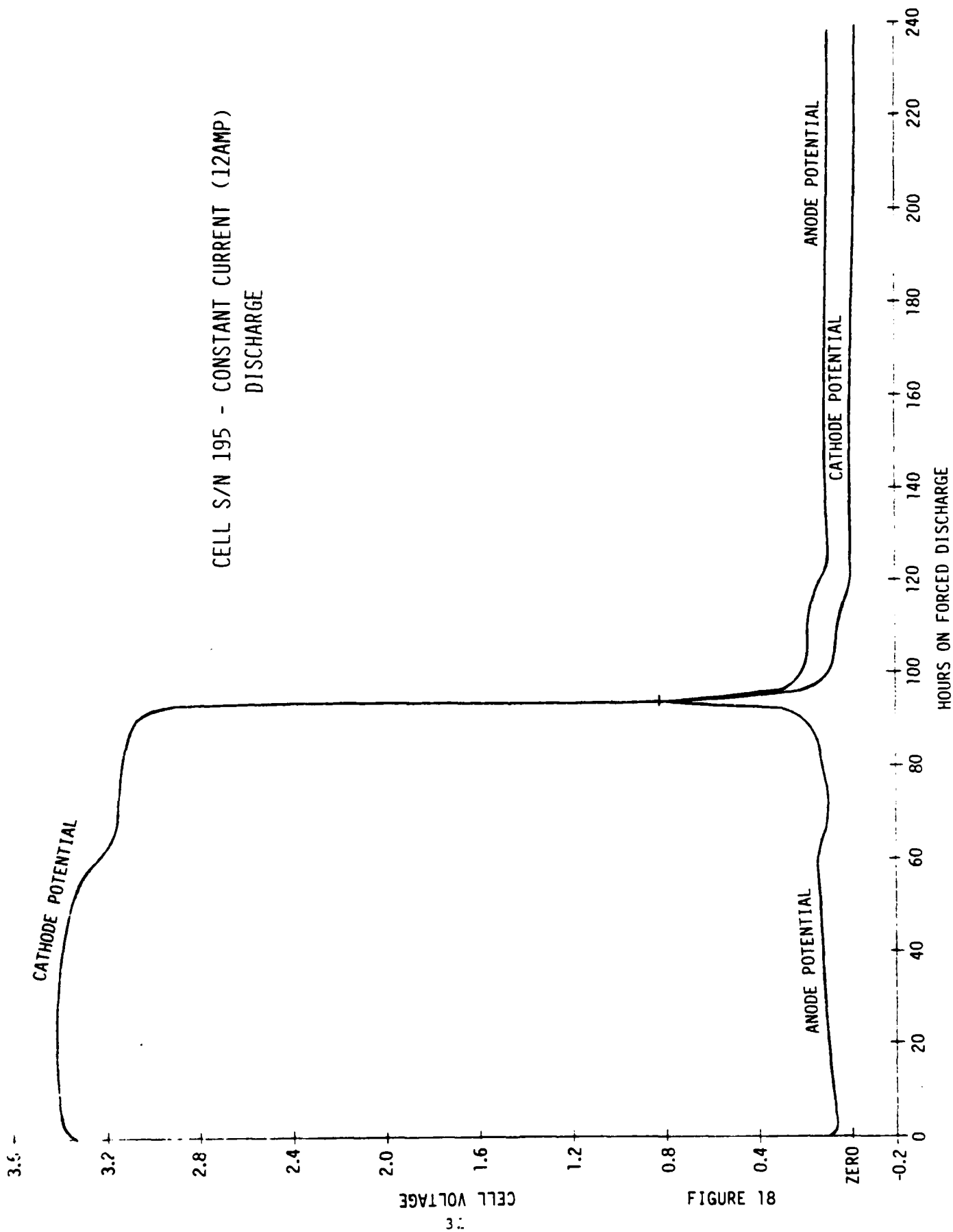


FIGURE 17



CELL S/N 195 - CONSTANT CURRENT (12AMP)
DISCHARGE

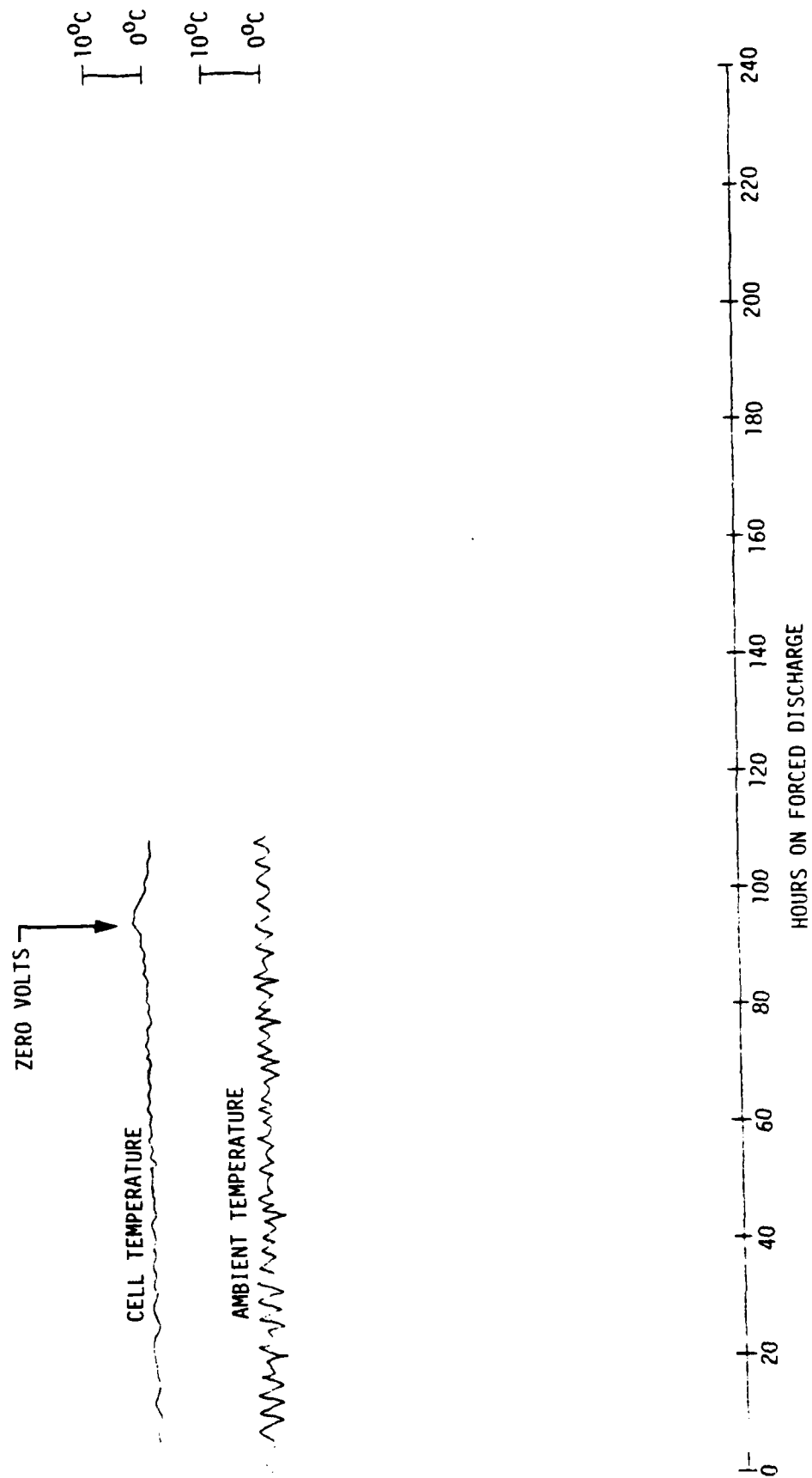
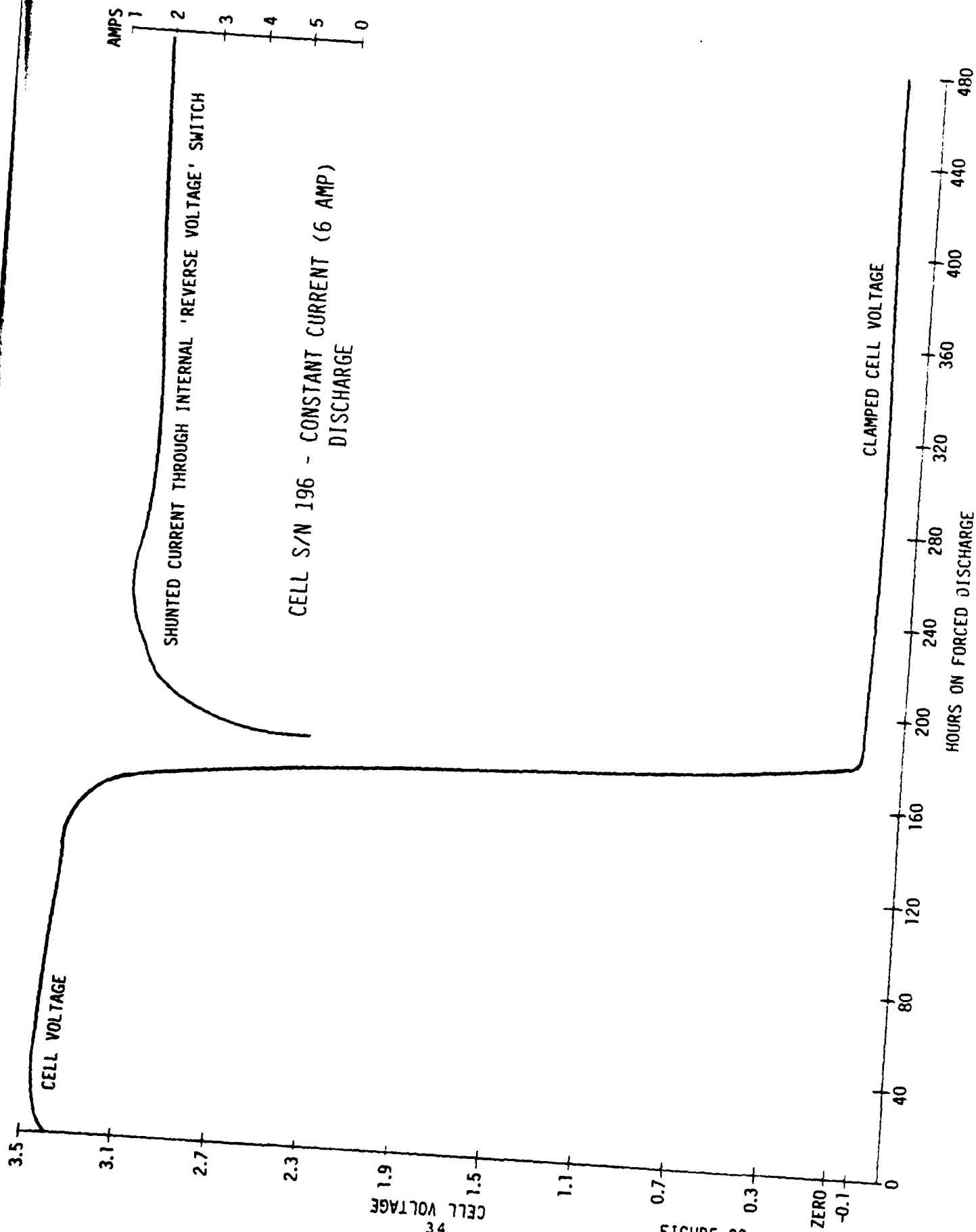
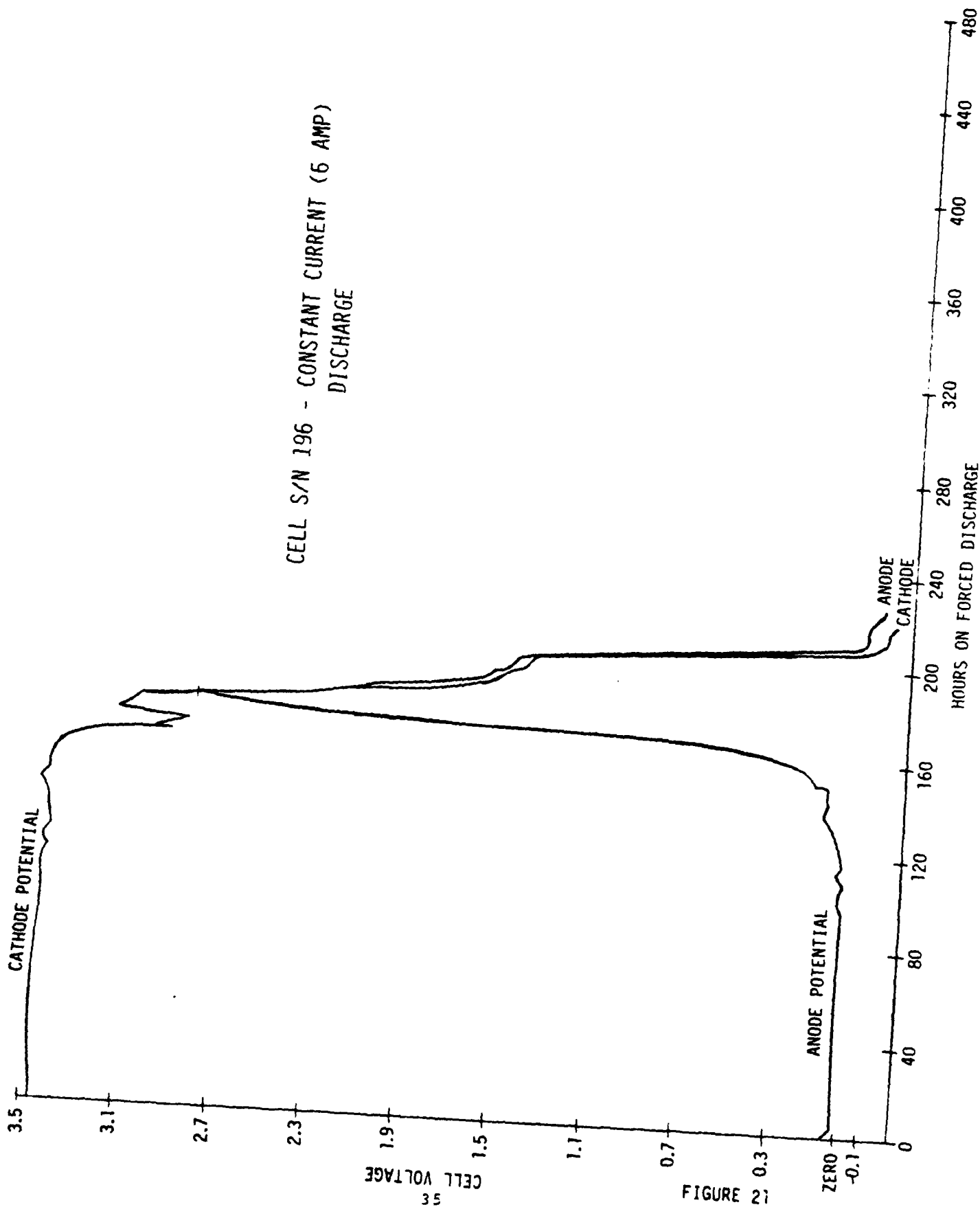


FIGURE 19





CELL S/N 196 - CONSTANT CURRENT (6 AMP) DISCHARGE

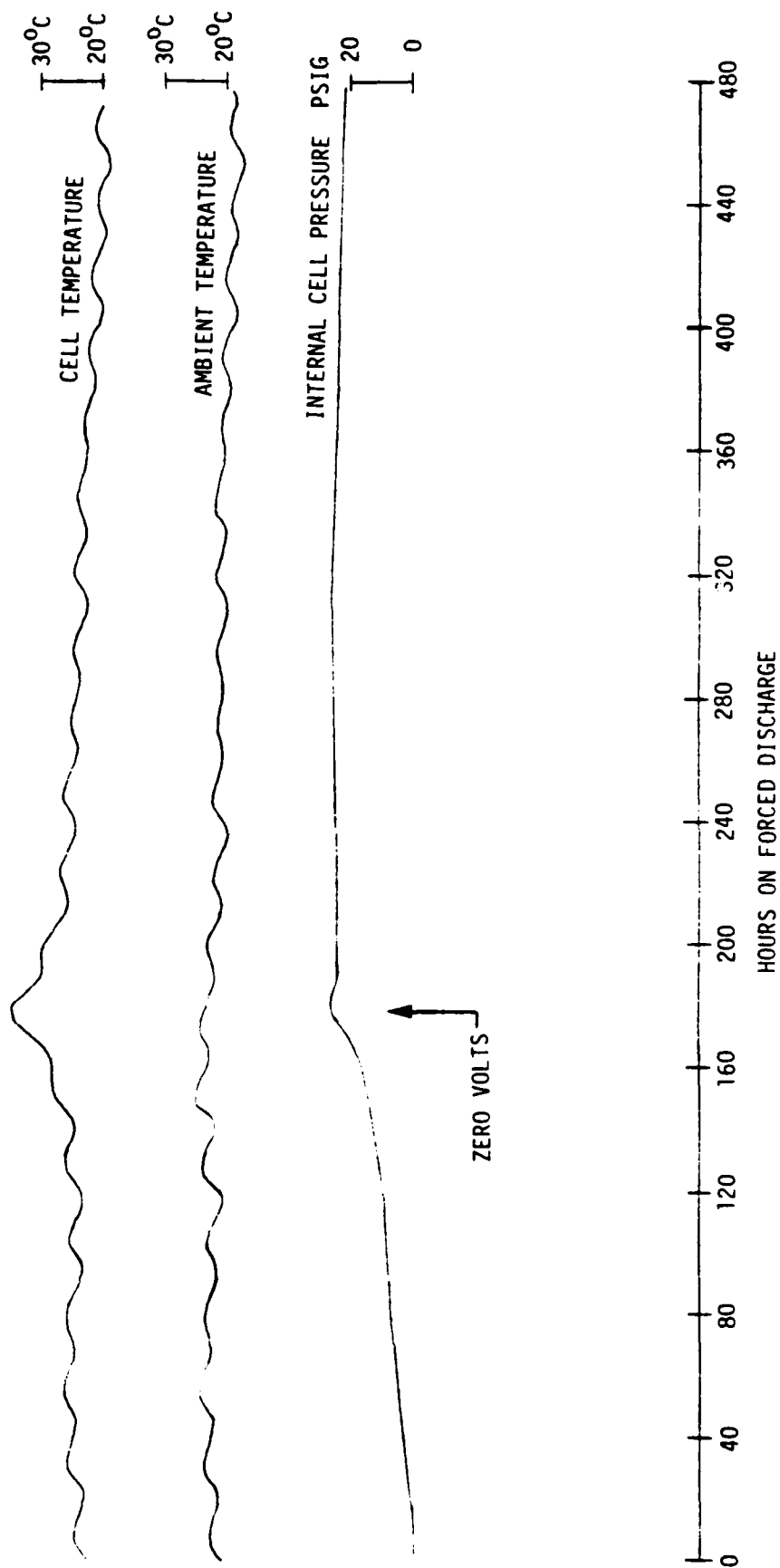
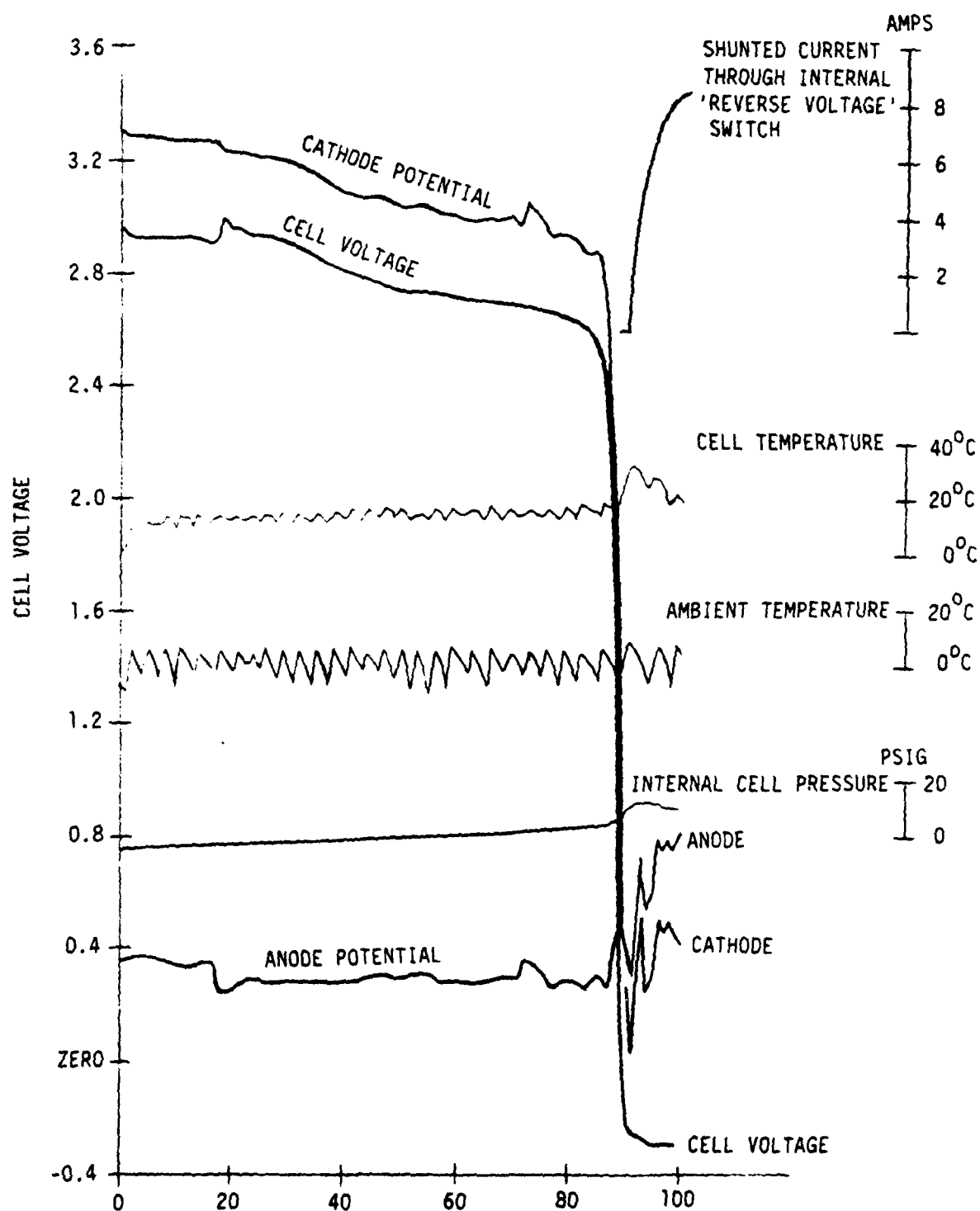


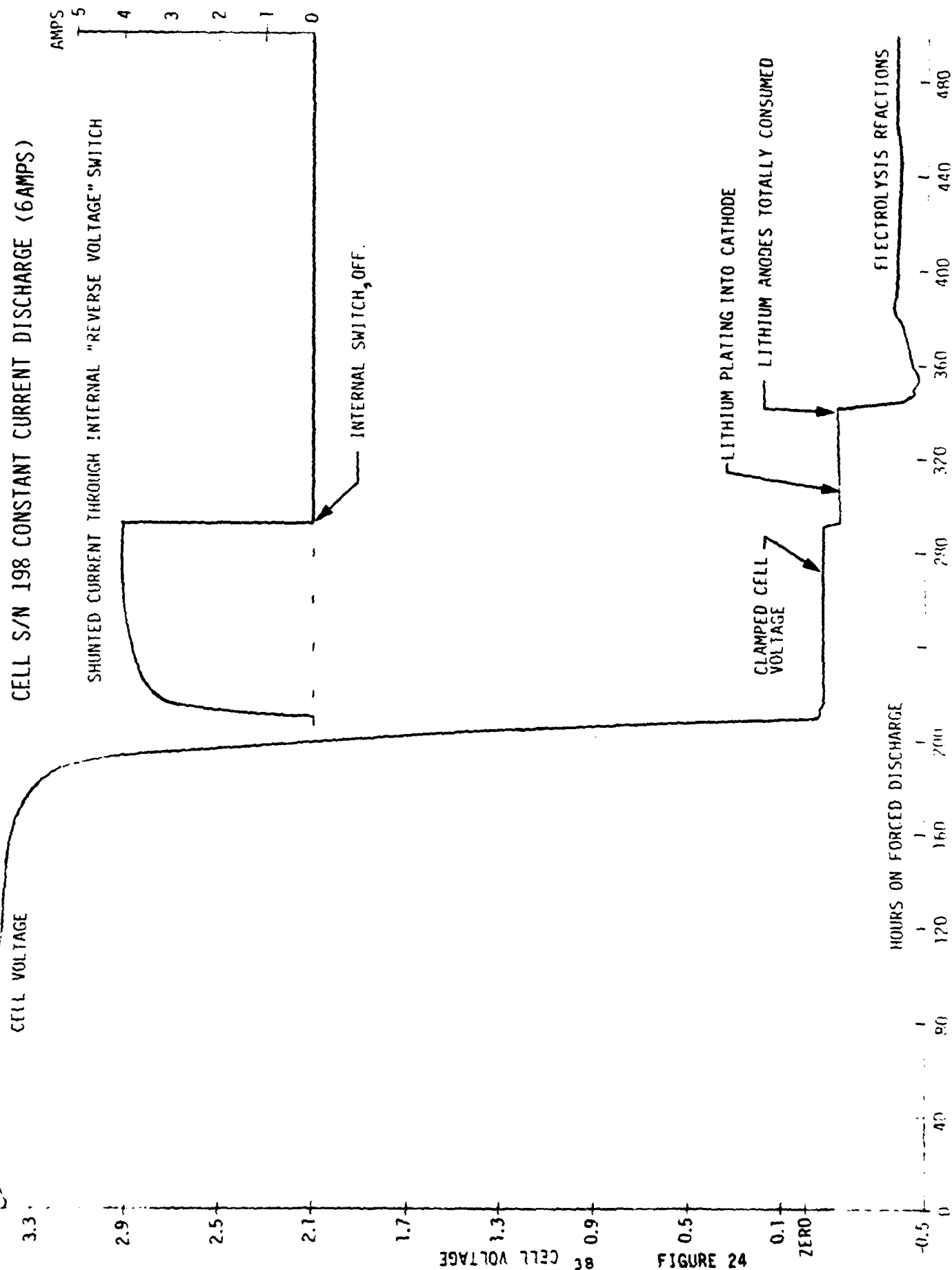
FIGURE 22

CELL S/N 197 - CONSTANT CURRENT (12 AMP) DISCHARGE



HOURS ON FORCED DISCHARGE

FIGURE 23



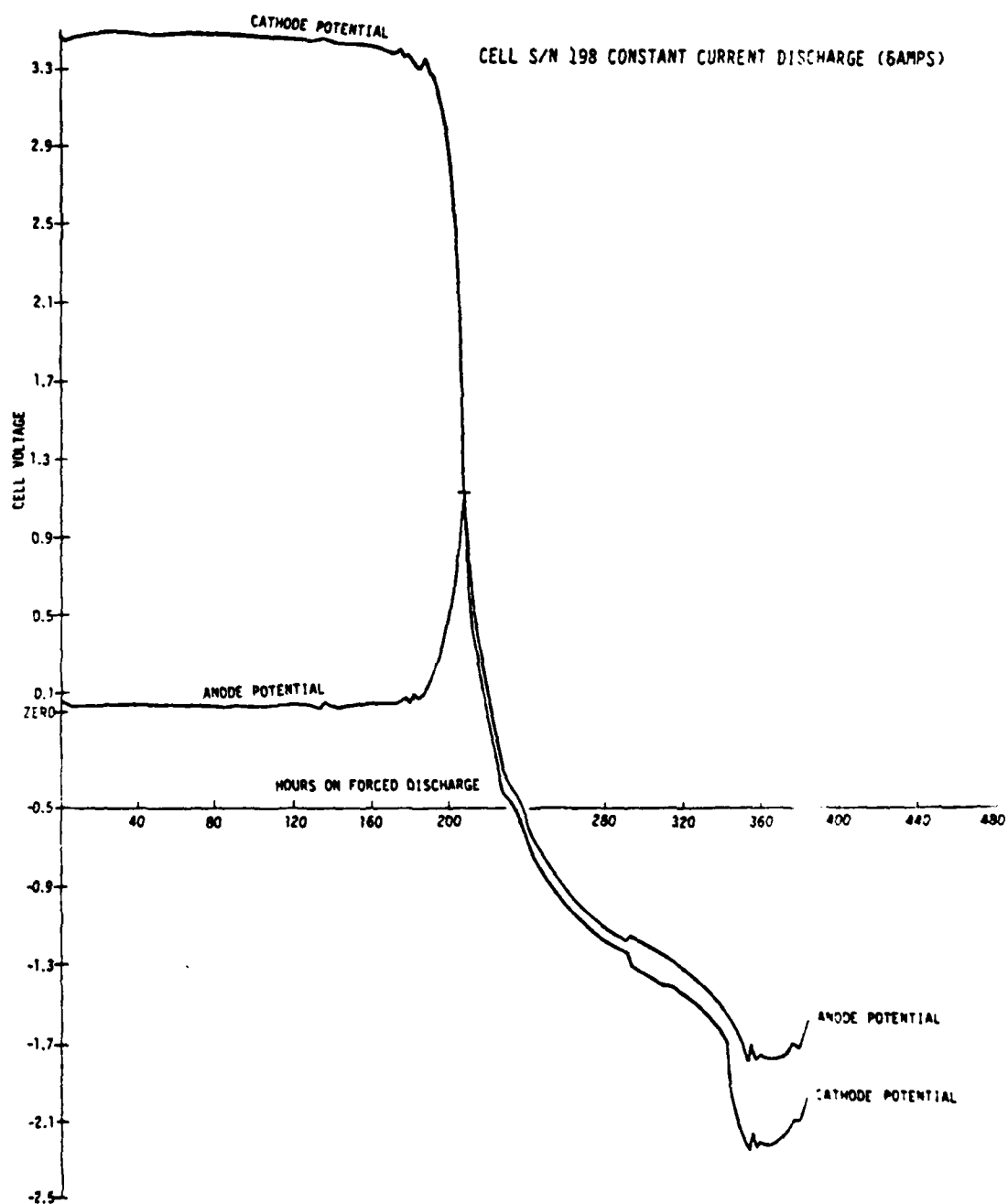


FIGURE 25

CELL S/N 198 CONSTANT CURRENT DISCHARGE (6AMPS)

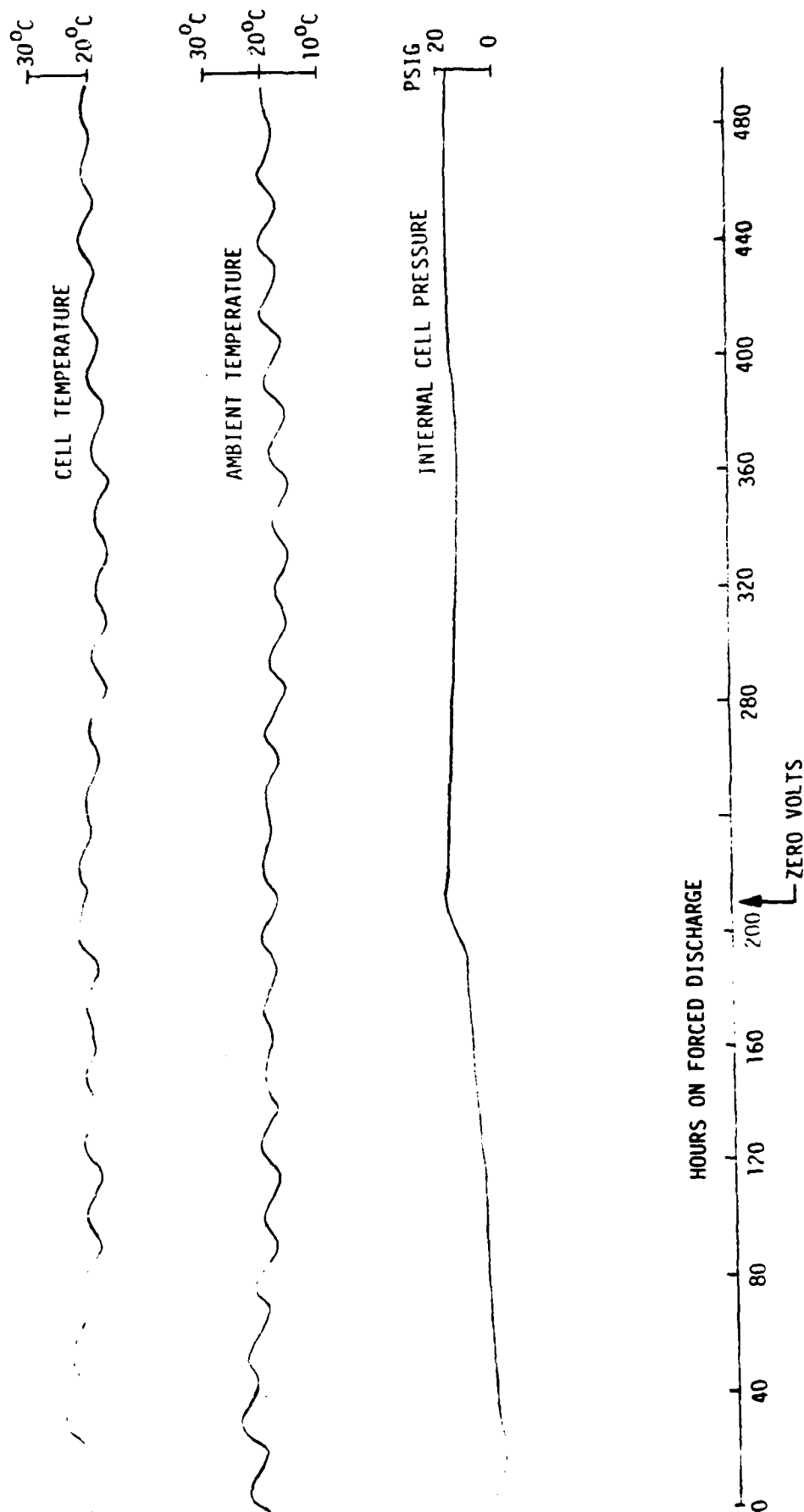
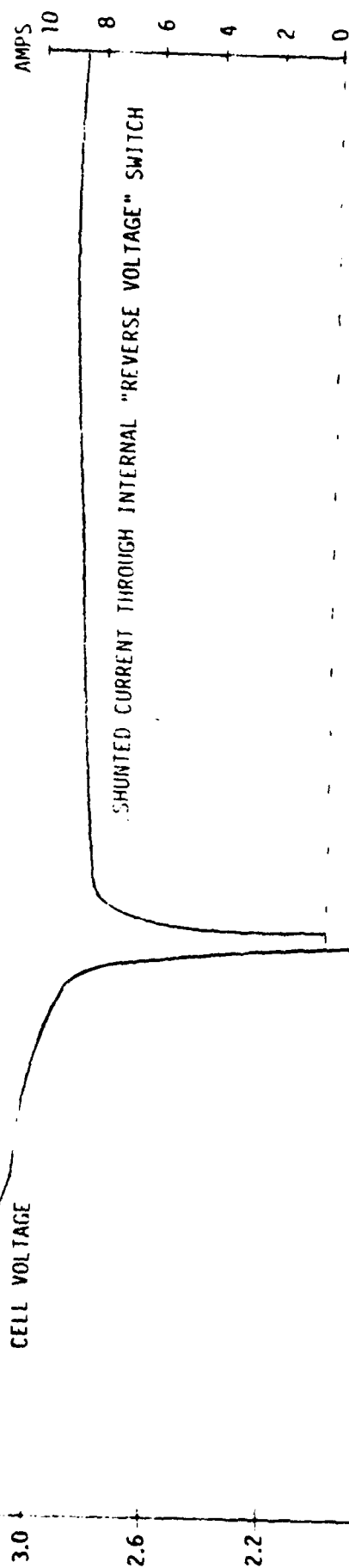


FIGURE 26

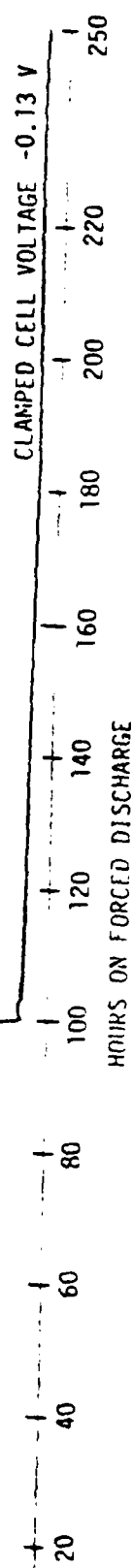
CELL S/N 199 - CONSTANT (12A) DISCHARGE AT 0°C



14 CELL VOLTAGE

FIGURE 27

ZERO



CLAMPED CELL VOLTAGE -0.13 V

CELL S/N 199 - CONSTANT (12A) DISCHARGE AT 0°C

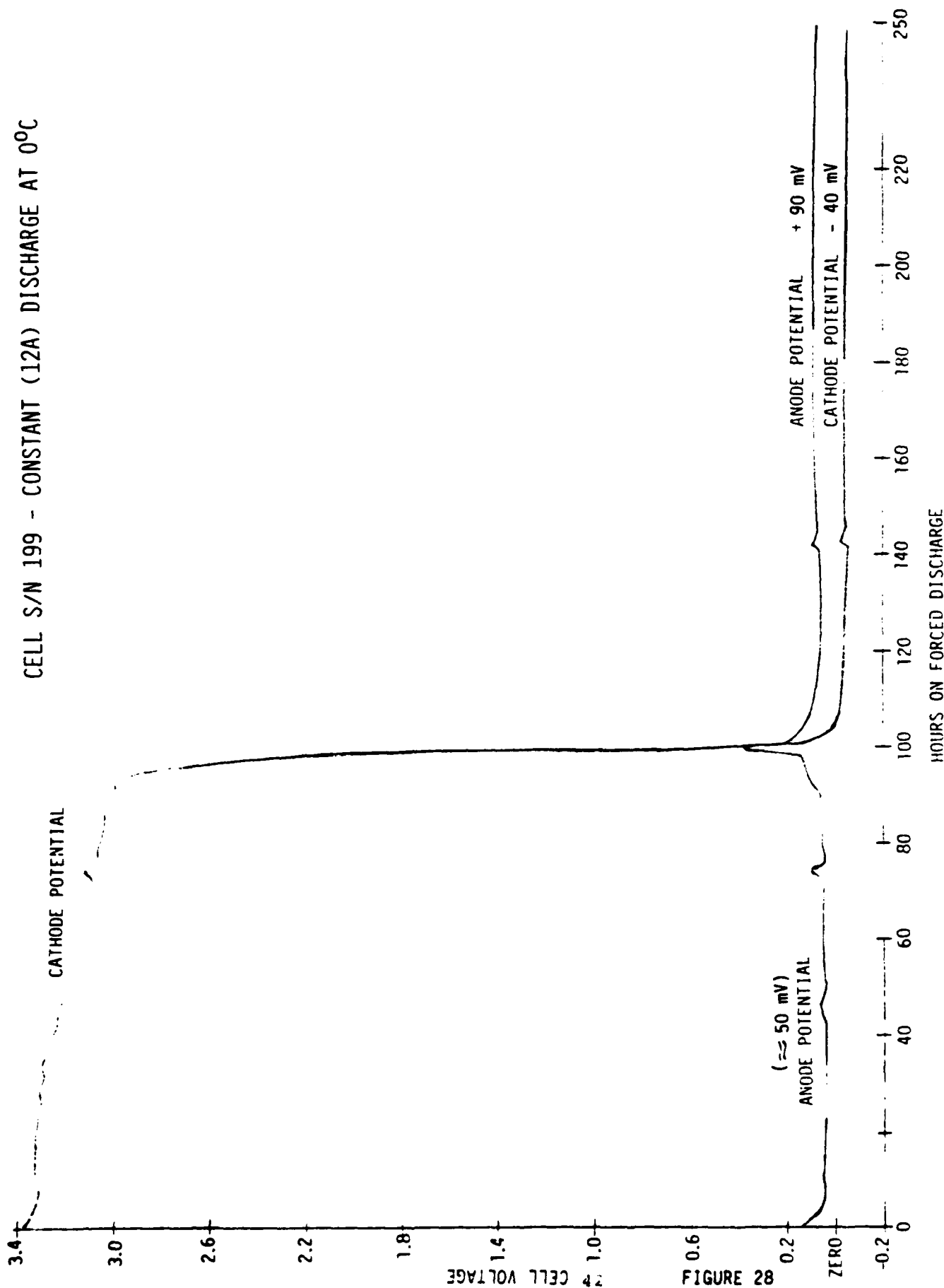


FIGURE 28

CELL S/N 199 - CONSTANT (12A) DISCHARGE

END OF CELL LIFE

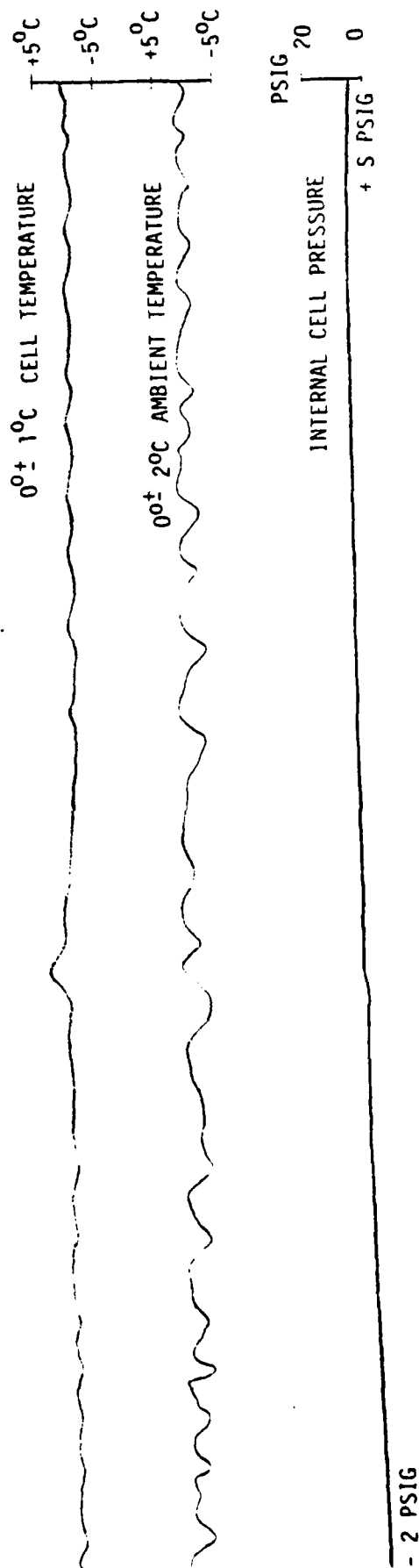
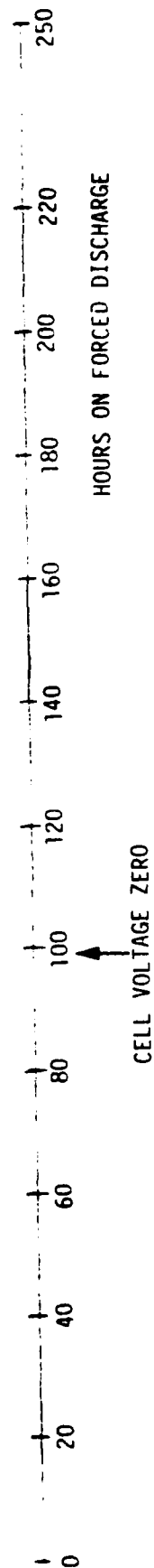


FIGURE 29
43



CAPACITY/DISCHARGE HOURS	#192		#193		#194		#195	
	Capacity AH	Hours Of Discharge	Capacity AH	Hours Of Discharge	Capacity AH	Hours Of Discharge	Capacity AH	Hours Of Discharge
To 3.0 volts	1249	209	1217	101	1233	209.5	959	80
To 2.7 volts	1267	212	1362	113	1242	211	1103	92
To 0.0 volts	1329	222.5	1428	118.5	1277	217	1139	95
Average Current	5.98 Amps		12.05 Amps		5.83 Amps		11.98	
AMB Temperature	27° ± 3°C		5° ± 5°C		26° ± 3°C		0.5° ± 3°C	
Reverse Voltage Capacity/HRS	2105 AH	354.5 HRS	2127 AH	176.5 HRS	2183 AH	374.5 HRS	2137 AH	177.5 HRS
Average RV Current	5.94 Amps		12.05 Amps		5.83 Amps		12.04 Amps	
Clamped Cell Voltage	-0.074 Volts		-0.122 Volts		-0.058 Volts		-0.120 Volts	
% Shunted Current	70%		68%		66%		67%	
Design Considerations	Cathode Limited (Standard Cathode Weight)				Severely Cathode Limited (Cathode Weight 80% Of Std.)			
Capacity Design	Std. Full Capacity (1400 AH Nominal)				80% Of Std. Capacity (1120 AH)			
% RV Demonstrated	>150% OF 1400 AH		>150% OF 1400 AH		>150% OF 1400 AH		>150% OF 1400 AH	

FIGURE 30

CAPACITY/DISCHARGE HOURS	#196		#197		#198		#199	
	Capacity AH	Hours Of Discharge	Capacity AH	Hours Of Discharge	Capacity AH	Hours Of Discharge	Capacity AH	Hours Of Discharge
	939	158.5	000	0.	1154	192.5	909	76
	953	161	821	68	1172	195.5	1136	95
	1053	178	1093	90.5	1257	210	1196	100
Average Current (To 3 V)	5.92 Amps		12.07 Amps		5.99 Amps		11.96	
AMB Temperature	21° ± 4°C		0° ± 5°C		21° ± 5°C		0° ± 2°C	
Reverse Voltage Capacity/HRS	2302 AH	392.5 HRS	121 AH	10 HRS	2185 AH	366. HRS	2262 AH	189. HRS
Average RV Current	5.87 Amps		12.07 Amps		5.97 Amps		11.97 Amps	
Clamped Cell Voltage	-0.069 Volts		-0.304 Volts		-0.066 Volts		-0.132 Volts	
% Shunted Current	68%		70%		70%		74%	
Design Considerations	Cathode Limited (Std. Cathode Weight) Heavy Duty RV Switch		Cathode Limited (Std. Cathode Weight) Normal RV Switch		Cathode Limited (Std. Cathode Weight) Normal RV Switch			
% RV Demonstrated	>150% Of 1400 AH		Test Completion Not Possible		>150% Of 1400 AH		>150% Of 1400 AH	

FIGURE 31

REVERSE VOLTAGE DATA

CELL S/N	192	194	196	198	193	195	199
CONSTANT FORCE DISCHARGE CURRENT	5.94 A	5.83 A	5.87 A	5.97	12.05 A	12.04 A	11.97
AMP HOURS ENDURED IN REVERSE-VOLTAGE BEFORE TEST TERMINATED	2105 AH	2183 AH	2302 AH	2185 AH	2127 AH	2137 AH	2262 AH
HOURS IN REVERSAL	355 H	375 H	393 H	366 H	177 H	178 H	189 H
CLAMPED NEGATIVE VOLTAGE	-0.074 V	-0.058 V	-0.069 V	-0.070 V	-0.122 V	-0.120 V	-0.132 V
% SHUNTED CURRENT THROUGH SWITCH	70%	66%	68%	70%	68%	67%	74%
ENVIRONMENTAL TEMPERATURE	27+3°C	26+3°C	21+4°C	21+5°C	5+°5C	0.5+3°C	0.+2°C
CELL TEMPERATURE	28+3°C	27+3°C	24+5°C	21+5°C	4+2°C	0°+1°C	0.+1°C
FINAL CELL PRESSURE	20 PSIG	18 PSIG	22 PSIG	17 PSIG	1 PSIG	NOT MEASURED	6 PSIG

FIGURE 32

6. Capacity

The capacity of each cell is summarized in Figures 30 and 31 for 3.0, 2.7 and 0.0 volt cut off. All of these capacity values are low compared to the normal 1400 AH to 3.0 volts at 6 amps/21°C or 1200 AH to 2.7 volts at 12 amps/0°C seen on previous production units. However the lower capacity at lower temperature (0°C) operation is consistent. The spread in capacity attained is also far wider than would be experienced with production units where ± 50 AH is more typical. Although capacity performance was not the main objective of this study, the results do require some explanation. The low capacity yielded can be attributed in general to the experimental nature of this study where significant design modifications were necessary to internally connect the reverse voltage switch and a reference electrode to the two extra and separate electrical feedthrough terminals. Cells S/N 194 and 195 were deliberately designed to be 20% low in capacity by the severe carbon cathode limitation.

Of the two series of cells manufactured, the second run of four cells (S/N 196 - 199) exhibited the lowest capacity and this has been attributed to the poorer quality of the batch of separator material used in their fabrication. The eight cells were fabricated in two lots of four each.

7. Technical Conclusions

The performance summaries are tabulated in Figures 30 and 31 for the series of 8 cells tested in this study. The reverse voltage performance is further tabulated in Figure 32 for reference.

With the exception of the faulty cell (197) the data are consistent for the cell operating voltage and individual anode and cathode potentials with respect to the Li/Li⁺ reference.

All cells were cathode (carbon) limited and with the internal RV switch operating there was sufficient lithium content to reliably exceed 100% voltage reversal for the 1400 AH cell. All the cells maintained a low internal pressure and there appeared to be no gas generated in RV. The data from cell 198 was interesting in that it emphasises the need to shunt the majority of the force discharge current in reverse voltage condition to avoid lithium limitation when higher negative voltages are reached and dangerous electrolysis reactions inevitably lead to cell venting.

The final design of HEDB cell represented in cells 198 and 199 will ensure a safety in reverse voltage for any condition which can possibly occur in a battery of series connected cells.

8. RECOMMENDATIONS

Over a 3-year period at Altus Corporation, development of a generic High Energy Density Battery for Navy use has progressed from early demonstration of unique safety features to recent perfecting of a reliable anode design and reliable internal reverse voltage switch. Two hundred cells have been tested over this period.

In this final phase of testing, eight cells were tested into reverse voltage under a variety of conditions, including a cell of marginal electrolyte fill and marginal voltage. All of these cells survived reverse voltage testing with no explosions and negligible internal pressure rise.

A reference lithium anode was used in all cells to separately monitor end of anode life and end of cathode life. The cathode limited condition of all cells was verified. A separate feed-thru pin in all cells allowed the measurement of the current shunted through the internal chemical switch that remains open in the forward direction and closes immediately upon cell reversal. Upon closing, the switch maintains a low clamped negative voltage of -50 to -100 millivolts and shunts 70% of the forced current. At the low negative voltage, dangerous plating potentials are avoided and the excess lithium is consumed by the remaining 30% of the current as it is plated into the cathode. This mechanism allows the cells to safely endure in excess of 100% of reverse voltage condition without external switches or circuits.

The basic cell design including the improved anode current collector is now fixed. The cell technology is ready for application in battery systems. The basic cell offers the advantage of ease of scalability to cells of different capacity and aspect ratios. The location of the terminals is optional. The cell case is hermetically sealed and has high vacuum integrity and no discharge products can escape to the exterior environment.

For applications where gravimetric energy density is a prime design parameter and exposure to high external pressure is not required, the cell case weight of 14 pounds can be reduced to 7 pounds for a total cell weight reduction from 29 to 22 pounds. For this lighter case, using precision welding techniques now available, the integrity of the hermetic sealed case can be maintained.

For operation in an unpressure-compensated ocean environment, the present cell, because of its unique pressure vessel design, and attitude insensitivity, can withstand up to 500 psi external pressure with no modification. The design is also amenable to minor mechanical strengthening for safe operation at even higher pressures.

LMED
-8